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ON TRIVALENT CARBON.

(FOURTH PAPER.)

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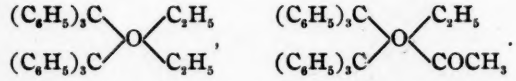
IT was shown in previous papers upon this subject that by the action of various metals upon triphenylchlormethane an extremely unsaturated hydrocarbon is produced, to which was assigned the constitution of triphenylmethyl, $(C_6H_5)_3C$. The hydrocarbon was found to unite very readily not only with atmospheric oxygen and with iodine, but also with a number of oxygen compounds, such as ethyl ether, acetic ester, etc. The simple oxygen compound was shown to possess the constitution of a peroxide, being formed by the direct addition of a molecule of oxygen to the unsaturated hydrocarbon:

$$\begin{array}{l} (C_6H_5)_3C \\ (C_6H_5)_3C \end{array} + \begin{array}{c} O \\ \| \\ O \end{array} = \begin{array}{l} (C_6H_5)_3C-O \\ \quad\quad\quad\quad | \\ (C_6H_5)_3C-O \end{array}.$$

This peroxide is a beautifully crystalline stable body, only very slightly soluble in the usual organic solvents, and shows none of the unsaturated properties of the original hydrocarbon. The ether and ester compounds, on the contrary, still possess the unsatura-

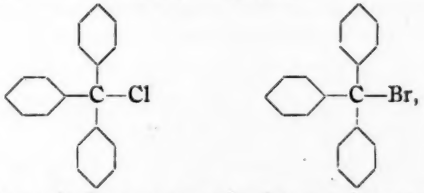
tion to the same extent as the hydrocarbon itself. Their solutions, when exposed to air, absorb oxygen almost as readily as triphenylmethyl itself, and also give the above-mentioned peroxide. The composition of these compounds was found to be 2 molecules of triphenylmethyl to 1 molecule of the ether or the ester. The theory was tentatively advanced[1] that the constitution of these bodies could best be explained by assuming the existence of tetravalent oxygen:



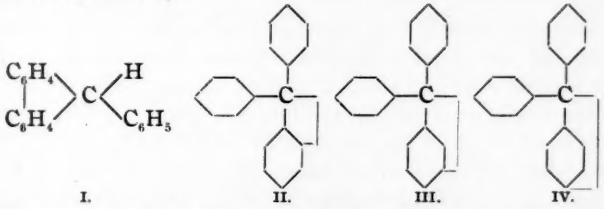
Experiments have since shown that this reaction of the hydrocarbon towards ethers and esters is quite general. Analogous compounds are formed with methylpropyl ether, ethylpropyl ether, methylbenzyl ether; with methyl acetate and other esters. Experimental data in favor of the existence of tetravalent oxygen were, at the time when the above formulas were proposed, very few. The principal support in favor of such a view was to be found in the physico-chemical studies of Brühl,[2] in the work of Collie and Tickle[3] upon the oxonium bases of dimethylpyron, and in the azoxonium bodies of Kehrmann.[4] Since the publication of my last paper, several important contributions in regard to the existence of tetravalent oxygen have been published. We should be quite justified at present, in the light of the recent work of Baeyer and Villiger,[5] Werner,[6] Walden,[7] Büllow and Sicherer,[8] and Kehrmann[9] to consider the existence of tetravalent oxygen as entirely probable, and to employ this probability as a support of the view as to the constitution of the ether and ester compounds of triphenylmethyl. Still, even at present, it seems best to adhere to the original plan: to place the constitution of triphenylmethyl itself upon an experimental basis first; after that we can employ this extremely unsaturated body for a further study of the valency of oxygen, and perhaps that of other elements.

[1] This Journal, **23**, 501.
[2] *Ber. d. chem. Ges.*, **28**, 2847, etc.
[3] *J. Chem. Soc.*, **75**, 710.
[4] *Ber. d. chem. Ges.*, **32**, 2610; **34**, 1623.
[5] *Ibid.*, **34**, 2679, 3612.
[6] *Ibid.*, **34**, 3300.
[7] *Ibid.*, **34**, 4185.
[8] *Ibid.*, **34**, 3916.
[9] *Ibid.*, **35**, 341, 343.

That the constitution of triphenylchlormethane and triphenylbrommethane is really as shown below,



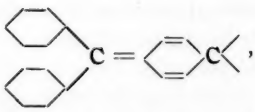
there can be no doubt, as was again shown quite recently by Kehrmann.[1] It is well known that metals may act upon halogen compounds in either of the two ways: (1) the halogen alone may be removed, and then 2 radicals unite into 1 molecule; (2) the metal may induce the splitting off of a halogen acid, and thus give rise to an unsaturated body. If metals affect triphenylchlormethane in such a way as to cause the removal of hydrochloric acid then the constitution of the resulting body may be expressed by one of the following four formulas:



I. II. III. IV.

A substance possessing constitution I has been prepared some time ago by Hemilian,[2] and also by E. and O. Fischer,[3] by the action of heat (250° C.) upon triphenylchlormethane. It is a stable, saturated hydrocarbon, and is different in every respect from the "triphenylmethyl" described by myself. Formulas II, III, and IV[4] give no adequate explanation why the hydrocarbon should be so very unstable and unsaturated. Because of these considerations I expressed myself as follows[5]: "Should it be proved at some future time that the action of metals upon triphenylchlormethane results, after all, in the elimination of hydrochloric acid, the behavior of the hydrocarbon will best be explained by the constitution

[1] *Ber. d. chem. Ges.*, **34**, 3818.
[2] *Ibid.*, **7**, 1208.
[3] *Ann. Chem.* (Liebig), **194**, 259.
[4] Norris: *Am. Chem. J.*, **25**, 122.
[5] *Am. Chem. J.*, **25**, 333.



involving the existence of bivalent carbon". Kehrmann,[1] in a recent paper, seems to give preference to this constitution, without, however, advancing any new experimental proofs.

It has, however, been assumed by me all along that metals in this instance do not split off hydrochloric acid, but only the chlorine, giving as a result the free radical, triphenylmethyl, $(C_6H_5)_3C$. One of the reasons for this assumption was the fact that by the action of iodine upon the unsaturated hydrocarbon a body of the composition $(C_6H_5)_3CI$ was obtained. As the yield was very small, only a few qualitative tests were made, and little could be said with certainty as to the mechanism of its formation. The reaction has now been studied in detail, and it will be shown that if certain conditions are observed it is possible to obtain triphenyliodomethane almost *quantitatively*. The iodocompound is an extremely unstable body, and the isolation of it in the dry state is attended with great difficulties. It was therefore prepared in most instances only in solution in some organic solvent, and the solution was at once used up for the experiments. I have made a comparative study of the reactions of triphenylchlormethane and triphenylbrommethane on one hand, and triphenyliodomethane on the other, with the result that the latter was found to be absolutely identical in its chemical behavior with the former two. The following reactions were studied: 1. Amount of iodine taken up by the hydrocarbon; 2. Reaction of the iodocompound with ammonia; 3. Reaction with substituted amines; 4. Formation of perhalides; 5. Empirical composition of the iodocompound; 6. Formation of double salts with the halide salts of metals.

1. TITRATION WITH IODINE.

Preparation of the Hydrocarbon.—The triphenylmethyl was prepared in the following way: 20 grams of triphenylchlormethane are dissolved in thoroughly dried benzene, and about 10 grams of zinc in the form of turnings or sticks are added to the solution. All the air in the flask must be completely displaced by

[1] *Ber. d. chem. Ges.*, **34**, 3815.

dry carbon dioxide. The solution at once turns yellow, and the metal soon becomes coated with a number of small droplets of a dark viscous mass. This syrupy material is a compound, in the nature of a double salt, of triphenylchlormethane with the zinc chloride which has been formed in the reaction. In five to fifteen days, depending upon the amount of the surface of zinc exposed, the reaction is completed. About 15 grams of the chlorocompound are reduced to the triphenylmethyl, while about 5 grams combine with the zinc chloride, forming a compound which is insoluble in benzene and which is therefore no further attacked by the metal. The benzene solution of triphenylmethyl is siphoned off from the zinc and the precipitated double salt, and is concentrated to a small bulk under diminished pressure. All the air must be rigorously excluded throughout the whole operation. If now to the very concentrated benzene solution acetic ester be added the ester compound will separate in a very short time in transparent, colorless crystals. By the addition of ethyl ether instead of the ester, the corresponding ether combination may be similarly obtained. If, however, acetone is added then one of the following two things will happen: If the solution still contains about 15 cc. of benzene then the triphenylmethyl will separate in combination with benzene, although the latter has become diluted with a large quantity of acetone; but if care has been taken to drive off all, or nearly all, the benzene before the acetone is added then the pure triphenylmethyl is obtained as a colorless, granulated precipitate. This tendency on the part of the hydrocarbon to enter into combination with benzene has been noticed in other instances, when solvents other than acetone are added to a concentrated benzene solution of the triphenylmethyl. It is peculiar that the combination of the hydrocarbon with benzene is in the same proportions as in the case of the ether and ester compounds: 2 molecules of the triphenylmethyl to 1 of the solvent.

A sample of the benzene compound obtained by the addition of acetone as described above, furnished on analysis the following results:

0.379 gram substance gave 1.2930 gram CO_2 and 0.2250 gram H_2O.

	Calculated for $2(C_6H_5)_3C + C_6H_6$.	Found.
Carbon	93.56	93.00
Hydrogen	6.44	6.59

A portion, 1.622 grams, was heated for some time in a stream of carbon dioxide at 80°-90° C., and the loss amounted to 0.2100 gram.

	Calculated for $2(C_6H_5)_3C + C_6H_6$.	Found.
Loss, as benzene....	13.83	12.94

The escaping vapors were condensed in a freezing-mixture and were identified as benzene by the melting-point, the characteristic odor, and the smoky flame. In another instance, a combustion of the condensed liquid was made and the results proved beyond doubt that it was benzene.

For the preparation of the pure triphenylmethyl in all subsequent work the benzene solution of the hydrocarbon was evaporated to dryness and the dry crystalline residue was heated for an hour in a vacuum at 60°-80° C. To the residue warm acetone was added and the mixture was kept at a temperature of boiling acetone for one-half hour. On cooling, the crystalline mass was filtered, washed several times with acetone, and dried in a stream of carbon dioxide.

1.4600 grams were heated for two hours at 80° C., then for three hours at 90° C., and the loss amounted only to 0.0005 gram.

0.3307 gram substance gave 1.1310 gram CO_2 and 0.1851 gram H_2O.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.74	93.28
Hydrogen.....	6.26	6.22

Triphenylmethyl when dry is a fairly stable substance. It may be exposed to air for a short time without danger of oxidation. It is white when freshly prepared, but soon turns pale yellow. It is soluble in benzene, carbon disulphide, only slightly soluble in acetone, and hardly at all in petroleum ether. While colorless itself, the solutions of triphenylmethyl are always yellow, no matter what solvent be employed. This phenomenon will be studied more fully later. The solutions of the hydrocarbon when exposed to air instantly become covered on the surface with a crystalline crust of the peroxide; in a short time the whole of the triphenylmethyl is converted into the oxidized product, and the supernatant liquid becomes colorless.

Titration.—Triphenylmethyl absorbs not only oxygen but also iodine. When a solution of the latter is added to that of the

former the iodine is absorbed instantly, the solution remaining pale yellow till nearly the end of the reaction. Many attempts have been made to make this a basis of a quantitative method for the estimation of the hydrocarbon, but owing to the instability of the triphenyliodomethane, only approximately quantitative results could be obtained. It will be seen from the reaction,

$$(C_6H_5)_3C + I = (C_6H_5)_3CI,$$

that the hydrocarbon requires 52.17 per cent. of its own weight of iodine for complete saturation. Similarly, when the acetic ester or the benzene compound are used for the titration it ought to proceed according to the equations

$$[(C_6H_5)_3C]_2.CH_3CO_2C_2H_5 + 2I = 2(C_6H_5)_3CI + CH_3CO_2C_2H_5,$$

$$[(C_6H_5)_3C]_2.C_6H_6 + 2I = 2(C_6H_5)_3CI + C_6H_6.$$

Accordingly, the ester compound should take up 44.2 per cent., and the benzene derivative 45 per cent. of iodine respectively for their complete saturation. The method of procedure was as follows: The substance to be titrated was placed in a flask from which all the air had been displaced by carbon dioxide. The substance was then either dissolved or just covered with a solvent, such as benzene, carbon disulphide, or petroleum ether, and a standard solution of iodine, from tenth-normal to half-normal, also in one of the above-mentioned solvents, was gradually added to the hydrocarbon. At the beginning, the halogen is taken up at once, the solution remaining pale yellow. After about 75-80 per cent. of the theoretical amount of the halogen has been added the absorption becomes noticeably slower and the solution grows darker in color; any further addition of halogen above 80-85 per cent. only tends to deepen the color. A large number of experiments were made in order to determine the cause why the reaction does not proceed smoothly to the end. Of the several explanations which have been thought of in this connection the following may be mentioned here as appearing, for the present, the most plausible: The triphenyliodomethane which is formed during titration is an exceedingly unstable body; when in solution it rapidly breaks down, being quite readily affected by light, and completely decomposed by atmospheric oxygen. When, in titration, about four-fifths of the triphenylmethyl is converted into the halogen derivative an equilibrium is apparently established; beyond this point any further

formation of the iodocompound will be checked by a corresponding decomposition with liberation of iodine.

The study of this halogen compound involves a great many difficulties, and anything like quantitative results can only be obtained by observing the strictest precautions, especially in regard to the exclusion of oxygen from the apparatus. In the following table is given a summary of the results obtained in this part of the work. The amounts of iodine indicated are those added until the pale yellow solution of the hydrocarbon just began to turn darker in color.

Substance employed.	Solvent.	Amount of substance. Grams.	Quantity of iodine taken up. Grams.	Per cent. of iodine taken up.	Per cent. of iodine required by theory.	Per cent. absorbed as compared with the theoretical amount.
Acetic ester compound	Benzene	5.1200	1.8132	35.41	44.20	80.10
Acetic ester compound	Benzene	2.9500	0.9967	33.78	44.20	76.50
Acetic ester compound	Benzene	2.8500	1.0014	35.21	44.20	80.00
Benzene compound	Benzene	1.3640	0.4760	34.17	45.00	77.50
Benzene compound	Carbon disulphide	2.0900	0.8252	39.00	45.00	86.70
Triphenylmethyl	Benzene	1.7380	0.6955	40.00	52.17	76.70
Triphenylmethyl	Benzene	2.0540	0.8620	42.00	52.17	80.40
Triphenylmethyl	Benzene	1.5150	0.6275	41.41	52.17	79.40
Triphenylmethyl	Carbon disulphide	1.5650	0.6874	43.92	52.17	84.10
Triphenylmethyl	Carbon disulphide	1.7060	0.7375	42.65	52.17	81.70

The table clearly shows that under the conditions above described about four-fifths, or somewhat more, of the hydrocarbon can be titrated without difficulty. All the solutions of the triphenyliodomethane obtained as given in the above table were at once used up for further experiments to be described below. In nearly every instance there was obtained some peroxide, which points to an incomplete saturation in the titration. Results considerably nearer to quantitative were obtained later in the work,

in the preparation of triphenyliodomethane in the dry state. The triphenylmethyl was covered with petroleum ether and warmed on the water-bath. To the warm mixture a standard solution of iodine in the same solvent was slowly added. The titration has to be carried on slowly, so as to prevent the separation of the triphenyliodomethane through the addition of the cold iodine solution. The end-reaction can be recognized fairly well. 2.3700 grams of triphenylmethyl took up 1.0342 grams iodine, which represents 83.60 per cent. of the theoretical amount. In working up this solution for triphenyliodomethane there was also separated nearly 0.300 gram of a mixture of the peroxide and some other body. By deducting this from the original 2.3700 grams, we see that the amount of absorbed iodine would be equivalent to 96 per cent. of the amount required by theory. In another instance, 2.4900 grams required 1.0710 grams iodine, or 82.4 per cent. of the theoretical amount. By subtracting 0.350 gram of non-halogen product found on working up the reaction mixture, we find that the amount of iodine actually taken up represents again almost 96 per cent. of the amount required by theory for pure triphenylmethyl. Further study of this question is necessary.

2. REACTION WITH AMMONIA.

It was shown by Elbs,[1] and by Hemilian and Silberstein,[2] that triphenylbrommethane reacts with ammonia and gives triphenylamine. The same reaction was carried out by Nauen[3] on triphenylchlormethane. I find that triphenyliodomethane reacts at *ordinary* temperature with ammonia, and the yield of the amine compound is almost quantitative.

4 grams of the acetic ester compound of triphenylmethyl were dissolved in benzene, and iodine added as described under titration. 1.4960 grams of the halogen were added. The solution was then placed in ice-water and dry ammonia was passed into the solution of the halogen compound. The separation of ammonium iodide began with the first few bubbles of the gas. The ammonium iodide was filtered off, the benzene solution concentrated to a small bulk, and to that alcohol was added. On cooling, the triphenylaminomethane crystallized almost pure, containing a small

[1] *Ber. d. chem. Ges.*, **17**, 703.
[2] *Ibid.*, **17**, 741.
[3] *Ibid.*, **17**, 442.

amount (0.150 gram) of the triphenylmethyl peroxide. It melted at 102° C., and agreed in every respect with the amine obtained from triphenylchlormethane in a parallel experiment. The yield was 2.6 grams, which represents 85 per cent. of the quantity required by theory. The calculation of the theoretical quantity of this and of the other amines must be made, of course, not upon the basis of triphenylmethyl used in the experiment, but only upon the amount of iodine added, because this alone determines the amount of triphenyliodomethane which is available in the reaction. For analysis, the amine was recrystallized from dilute alcohol.

0.2090 gram substance gave 0.6762 gram carbon dioxide and 0.1186 gram water.

0.2825 gram substance gave 14.9 cc. nitrogen at 23.5° C. and 748 mm.

	Calculated for $(C_6H_5)_3C.NH_2$.	Found.
Carbon	87.97	88.24
Hydrogen	6.63	6.31
Nitrogen	5.41	5.71

In another experiment 2.09 grams of the benzene compound of triphenylmethyl took up 0.8252 gram iodine and gave 1.995 grams of the almost pure amine, while the calculated quantity should have been 2.005 grams. One recrystallization from ether sufficed to furnish an absolutely pure product.

For further identification of the amine, the hydrochloride of it was prepared, which, on boiling with water, was converted into triphenylcarbinol, just as is the amine obtained by Elbs from triphenylbrommethane. The platinum double salts of the two amines were compared and were also found to be identical. There can be no doubt that the reaction above described takes place quantitatively according to the equation

$$(C_6H_5)_3CI + 2NH_3 = (C_6H_5)_3CNH_2 + NH_4I.$$

3. REACTION WITH SUBSTITUTED AMINES.

Triphenylchlormethane and triphenylbrommethane[1] react not only with ammonia but also with substituted amines, and give the corresponding substituted triphenylaminomethanes. The iodo-compound obtained by the addition of iodine to the unsaturated hydrocarbon behaves in every way similarly. It gives the identical substituted amines. While the reaction takes place quite readily

[1] Elbs: *Loc. cit;* Hemilian: *Loc. cit.*

and with good yield, with all the amines tried, by far the best results were obtained with para-toluidine. In this latter case the product obtained is at once pure, and the yield is as nearly quantitative as could be desired.

Triphenylmethylethylamine, $(C_6H_5)_3C.NH(C_2H_5)$. — 2.850 grams of the acetic ester compound of the hydrocarbon absorbed 1.001 grams of iodine. To this solution a little more than the theoretical amount of ethylamine in benzene was added. The reaction took place at once. On concentrating the filtered benzene solution of the amino-compound the latter separated as an oil which did not solidify until after several days' standing in a vacuum desiccator. The amine was dissolved in absolute ether, and precipitated as the hydrochloride by means of dry hydrochloric acid gas. In order to obtain the free base the salt was finely broken up under dilute alcoholic ammonia, filtered, washed with dilute alcohol and with water, and dried. Obtained in this way it is a white granular powder. When dissolved in any solvent it shows a great tendency to separate as an oil, which begins to crystallize only after some standing, or on introducing a crystal of the substance into the solution. When purified in this way it gives a melting-point of 75°-77° C. It behaves in every way as the simple triphenylaminomethane. It forms salts which suffer partial hydrolysis when dissolved in water, and which on boiling are completely decomposed with formation of triphenylcarbinol.

0.2995 gram substance gave 14 cc. nitrogen at 19° C. and 745 mm.

	Calculated for $(C_6H_5)_3CNH(C_2H_5)$.	Found.
Nitrogen.....	4.91	5.34

A sample of the same ethylamine compound was also prepared from pure triphenylchlormethane, and this was found to be absolutely identical with the one obtained from the iodo-compound in all its reactions, as well as in the tendency to separate from solvents in the form of an oil.

In the formation of this amine the reaction therefore proceeds as follows:

$$(C_6H_5)_3CI + 2C_2H_5NH_2 = (C_6H_5)_3CNH.C_2H_5 + C_2H_5NH_2.HI.$$

Triphenylmethylpropylamine, $(C_6H_5)_3C.NHC_3H_7$.—This body was prepared in a manner analogous to that which furnished the

ethylamine derivative. It, also, possesses the tendency to remain oily. After standing in a vacuum desiccator for some time the oil solidifies to a solid crust of crystals. These can be purified by spreading them out upon a porous plate and washing first with petroleum ether, then with a little alcohol. The substance melts at 70° C.

0.2230 gram substance gave 11.5 cc. N at 27° C. and 741 mm.

	Calculated for $(C_6H_5)_3CNHC_3H_7$.	Found.
Nitrogen	4.65	5.06

The hydrochloride is easily formed by passing dry hydrochloric acid gas into an ethereal solution of the base. On boiling the base or the salt with dilute hydrochloric acid it decomposes, and triphenylcarbinol is produced, a reaction which is common to all the amines of triphenylmethyl,

$$(C_6H_5)_3CNHC_3H_7 + H_2O = (C_6H_5)_3C.OH + NH_2C_3H_7.$$

Triphenylmethylamylamine, $(C_6H_5)_3C.NH(C_5H_{11})$. — Amylamine acts upon the iodine compound apparently somewhat slower than the other amines mentioned, and the reaction is best hastened by gentle heat. The substance was obtained as an oil, and all attempts to bring it to crystallization have failed. It was therefore analyzed in the form of its hydrochloride, which was prepared in the same way as the salts of the other bases here described. The oil itself was also analyzed and gave results which indicate that it was pure triphenylpropylamine.

0.2300 gram substance gave 9.1 cc. N at 25° C. and 740 mm.

	Calculated for $(C_6H_5)_3CNHC_5H_{11}$.	Found.
Nitrogen	4.20	4.29

The oil was boiled with dilute hydrochloric acid, and the triphenylcarbinol obtained was of such purity as to require no further treatment for analysis. It melted as obtained at 159° C. Consequently the oil was pure triphenylmethylamylamine.

Triphenylmethylaniline, $.(C_6H_5)_3C.NH(C_6H_5)$.—The reaction with aniline is very smooth; the resulting amine is produced in almost quantitative yield and is easily obtained pure. The experiment was repeated several times, and in no case was there noticed the formation of any other products than that of the aniline base and of some triphenylmethyl peroxide. In several instances the amount of aniline hydriodide formed in the reaction was also

determined, and was found to correspond exactly to the quantity of iodine added in the formation of the triphenyliodomethane. The yield of the aniline base, as well as that of the aniline salt, leaves no doubt that all the iodine added to the triphenylmethyl is used up in the formation of triphenyliodomethane, and that the reaction with aniline proceeds strictly according to the equation

$$(C_6H_5)_3CI + 2C_6H_5NH_2 =$$
$$(C_6H_5)_3CNHC_6H_5 + C_6H_5NH_2.HI.$$

In one experiment there was formed 14.5 grams of the crude aniline base while the amount required by theory was 16 grams. The product was divided into several portions and each purified by recrystallization from different solvents. The resulting products were all found to be identical, all melting at the same temperatures, namely at 149°-150° C. As Elbs gives the melting-point for the aniline base which he obtained from the triphenylbrommethane as 146° C., and as Hemilian gives it as 144.5° C., I prepared a sample of triphenylmethylaniline from carefully purified triphenylchlormethane, and found that it melts at 149°-150° C.

In another experiment 12 grams of the acetic ester compound of triphenylmethyl absorbed 4.3 grams iodine, and gave 9 grams of the aniline body. The latter was dissolved in ether and filtered in order to remove the small amount of triphenylmethyl peroxide mixed with the aniline base. On the addition of alcohol to the concentrated ethereal solution the triphenylmethylaniline crystallized in snow-white little prisms, possessing a melting-point of 148° C. The yield was 6.5 grams.

0.4607 gram substance gave 1.5010 grams CO_2 and 0.2697 gram H_2O.

0.4395 gram substance gave 17 cc. N at 22° C. and 729 mm.

0.3115 gram substance gave 12.2 cc. N at 19° C. and 742 mm.

	Calculated for $(C_6H_5)_3C.NH.C_6H_5$.	Found. I.	Found. II.
Carbon	89.53	89.98	....
Hydrogen	6.26	6.40	....
Nitrogen	4.18	4.25	4.27

The base obtained from the iodo-compound agreed in every respect with that made from the corresponding chlor- and brommethane. On treatment with amyl nitrite it gave the nitroso derivative which, when heated slowly, was found to melt at 156° C., as given by Elbs.[1]

1 *Ber. d. chem. Ges.*, **17**, 704.

Hemilian and Silberstein[1] state that when a benzene solution of triphenylmethylaniline is treated with hydrochloric acid gas it is decomposed even by the first few bubbles according to the equation

$$(C_6H_5)_3CNHC_6H_5 + HCl = (C_6H_5)_3C.Cl + C_6H_5NH_2.$$

This is correct in so far as a benzene solution of the base is concerned. But, curiously enough, if the benzene is diluted with absolute ether, or better still, if ether alone is employed as a solvent, then there is hardly any decomposition,—the base separates quantitatively as the hydrochloride salt. By this means the base can be readily and completely freed from the accompanying non-basic impurities.

Triphenylmethyl-o-toluidine, $(C_6H_5)_3C.NHC_6H_4CH_3$.—On the addition of orthotoluidine to a freshly prepared solution of triphenyliodomethane the reaction takes place at once. The hydriodide of the toluidine separates readily in the form of fine silky needles. On the addition of alcohol to the concentrated benzene solution the base is precipitated as an oil, which, however, soon changes to a crystalline mass. The crystals are dissolved in chloroform and separated by filtration from a little insoluble triphenylmethyl peroxide. On the addition of alcohol to the concentrated chloroform solution the triphenylmethyltoluidine crystallizes out pure, the crystals melting at 140° C., while the absolutely pure substance should melt at 142° C. The yield is about 80 per cent. of the calculated quantity. In one experiment, the base was obtained in a very pure state by precipitating the original benzene solution by means of ether instead of with alcohol, the subsequent purification being the same as before,—from a mixture of chloroform and alcohol.

0.2318 gram substance gave 8.9 cc. at 16.5° C. and 745 mm.

	Calculated for $(C_6H_5)_3CNH(C_7H_7)$.	Found.
Nitrogen.....	4.01	4.22

The preparation of the salts of this base is accompanied with very great difficulties, as has already been noticed by Elbs. In this respect this body behaves differently from the aniline compound. Hydrochloric acid gas decomposes quantitatively not only a benzene solution, but also an ethereal solution of the toluidine body:

$$(C_6H_5)_3CNHC_7H_7 + HCl = (C_6H_5)_3C.Cl + C_7H_7NH_2$$

[1] *Ber. d. chem. Ges.*, **17**, 747.

Triphenylmethylmetatoluidine, $(C_6H_5)_3C.NH(C_6H_4CH_3)$, is formed when metatoluidine is added to a solution of triphenyliodomethane. The reaction is, however, much slower than in the formation of the above-described amines. The purification of the base cannot be done without considerable loss of material, as it is quite soluble in the usual solvents.

Triphenylmethylparatoluidine, $(C_6H_5)_3C.NH(C_6H_4CH_3)$.—Of all the amino-compounds tried, paratoluidine furnished the most satisfactory results. The product is very easily obtained pure, and the yield is fully 90 per cent. of the theory.

5.12 grams of the acetic ester compound of triphenylmethyl required for apparent saturation 1.8132 grams of iodine. 5 grams of para-toluidine in benzene were added to the solution of the iodo-compound; the reaction took place at once, at ordinary temperature. The toluidine hydriodide was removed by filtration, washed with benzene, dried, and weighed. The quantity found was 3.2 grams, while the calculated amount should have been 3.35 grams. The benzene solution was concentrated under reduced pressure, and to the residue a mixture of alcohol and ether was added. As triphenylmethyl-*p*-toluidine is only sparingly soluble in either of those two solvents it crystallized out at once pure, leaving the excess of toluidine in solution. The yield of the base was 4.55 grams, while the quantity calculated from the amount of iodine added should have been 5.003 grams; the actual yield, therefore, of the pure product was 90 per cent. of the theory. In a second experiment, 4 grams of the toluidine base were obtained, against 4.4 grams as calculated, which is equivalent to 91 per cent. of the theory.

For analysis the substance can be recrystallized from ether, or from a mixture of chloroform and alcohol. By either method it can be obtained in beautiful large transparent crystals, melting, as given by Elbs, at 177°-178° C.

0.3138 gram substance gave 1.0329 gram CO_2 and 0.1898 gram H_2O.

0.4496 gram substance gave 15.6 cc. nitrogen at 25° C. and 735 mm.

0.4617 gram substance gave 18.6 cc. nitrogen at 26° C. and 716 mm.

	Calculated for $(C_6H_5)_3CNHC_7H_7$.	Found. I.	II.
Carbon	89.39	89.77	....
Hydrogen	6.65	6.71	....
Nitrogen	4.01	4.31	4.25

4. FORMATION OF PERHALIDES.

It was reported by me[1] some years ago that on the addition of iodine to a solution of triphenylbrommethane a periodide is formed. The body possessed the appearance and properties of the periodides of organic bases. The analyses led me to the conclusion at that time that the composition of the body was $(C_6H_5)_3CBr.I_4$. I also described[2] a perbromide, the composition of which was found to be $(C_6H_5)_3CBr.Br_5$. Nef[3] reported that he got a perbromide of a composition similar to the periodide. As no figures of analysis are given by him it was to be interpreted[4] that he had a tetrabromide, $(C_6H_5)_3CBr.Br_4$. In analyzing the periodide which was made from triphenyliodomethane it was found that it had the composition $(C_6H_5)_3CI.I_5$. I have, therefore, decided to go over the whole work on the perhalides of triphenylmethane. It may be now considered established that there is a strict uniformity in composition in all these substances—they are all pentahalides.

Triphenylbrommethane Pentabromide, $(C_6H_5)_3CBr.Br_5$.—Triphenylbrommethane is dissolved in as little chloroform as possible and the calculated quantity of bromine is added. On cooling, the perbromide separates in dark orange crystals. These are rapidly filtered off, dried on a porous plate in soda-lime desiccator, and are analyzed at once. The total bromine was estimated by Carius' method; the "perbromine" was estimated by suspending weighed amounts of the perhalide in a solution of potassium iodide in water, adding some chloroform, and titrating the iodine set free by the "perbromine". Several samples were analyzed.

0.5569 gram substance gave total 0.8935 gram AgBr.

0.2712 gram substance gave 0.1548 gram perbromine.

0.3121 gram substance gave 0.1761 gram perbromine.

	Calculated for $(C_6H_5)_3CBrBr_5$.	Found. I.	II.
Total bromide	66.42	67.23	....
Perbromine	55.32	55.04	56.4

[1] This Journal, **20**, 790.

[2] *Ibid.*, **20**, 1776.

[3] *Ann. Chem.* (Liebig), **308**, 304.

[4] Beilstein: Ergänzungsband II, 127.

The perbromide is very unstable, losing bromine very readily, even in a desiccator, the residue consisting of pure triphenylbrommethane. It can, however, be kept without decomposition for a considerable length of time in a tightly closed bottle.

Triphenylbrommethane Pentiodide, $(C_6H_5)_3CBr.I_5$.—This can be prepared by the addition of the calculated quantity of iodine dissolved in benzene to a solution of triphenylbrommethane. The periodide separates as an oil which in a few seconds becomes crystalline. The yield is usually from 75 to 80 per cent. of the calculated quantity. The periodide is much more stable than the corresponding perbromide. It can be kept in a desiccator for days without any appreciable loss of iodine. It is only slightly soluble in benzene and in carbon disulphide, is quite soluble in ether, probably with decomposition. All the iodine can be titrated with standard thiosulphate solution in water, the bromide being at the same time converted into the carbinol.

The total halogen was estimated by reducing the perhalide in ether by means of a dilute solution of sulphurous acid in water, making the solution slightly alkaline, and then boiling the mixture for one-half hour in order to insure the complete conversion of the bromide into the carbinol. The solution of the sodium iodide and bromide is filtered from the carbinol and the total halogen estimated with silver nitrate. A large number of samples of this body were prepared under slightly varying conditions, in order to ascertain positively its composition. The best results were obtained by adding a *warm* solution of iodine to a *warm* solution of the bromide. Either benzene or carbon disulphide may be used as a solvent.

I. Sample from benzene:
0.6930 gram substance gave 0.4523 gram iodine.
0.6085 gram substance gave 0.3975 gram iodine.
0.7895 gram substance gave 1.1015 grams AgBr+AgI.

II. Sample from carbon disulphide:
0.5000 gram substance gave 0.3312 gram iodine.
0.4210 gram substance gave 0.2739 gram iodine.
0.4455 gram substance gave 0.2917 gram iodine.
0.6550 gram substance gave 0.9125 gram AgBr+AgI.

	Calculated for $(C_6H_5)_3CBr.I_5$.	Found. I.		II.		
Iodine ...	66.25	65.25	65.43	66.20	65.05	65.48
Bromine .	8.41	7.90	....	7.85	....	....

The periodide is of a dark blue iridescent color. It melts at 92° C. It is quite probable that triphenylbrommethane may also give rise to lower periodides. The one reported by me as the tetraiodide was described as having a melting-point of 121° C.; and I once came across a periodide, also at this time, which melted at 120° C.

That we have here a true periodide of triphenylbrommethane, and that iodine did not replace bromine, is proved by the following two facts: First, some of the periodide was heated at 70°-80° C. until all the iodine was driven off; the residue was recrystallized from petroleum ether, and the product was found to be pure triphenylbrommethane. Second, some of the periodide was dissolved in ether and the solution was shaken with molecular silver until the color of iodine had just disappeared; on concentrating the filtered ethereal solution and recrystallizing the residue, pure triphenylbrommethane was again obtained.

Triphenyliodomethane Pentiodide, $(C_6H_5)_3I.I_5$.—This periodide is formed just as readily, if not more so, as the one described above. Indeed, it is even liable to be formed to some extent when triphenylmethyl is being titrated with iodine, unless the latter is added slowly. The hydrocarbon, or the ester or ether derivative of it, is dissolved in benzene or in carbon disulphide, and a solution of iodine in the same solvent is added until the end-reaction of the titration is reached. The solution is now gently warmed and more iodine is slowly added, with constant stirring, until the whole of the calculated amount is introduced. The periodide separates in fine shining needles, dark blue in color, and cannot be told by its appearance from the periodide of triphenylbrommethane. It is filtered, washed with a little benzene, and dried in a vacuum desiccator. Unlike the hydrocarbon, or the normal triphenyliodomethane, the periodide is stable, and can be exposed to dry air without fear of oxidation. The yield of the pure product is from 75 to 80 per cent. of the calculated amount, one part of triphenylmethyl furnishing three times its weight of the periodide. It melts at 90° C.

The total halogen is estimated, according to the method described under the periodide of the triphenylbrommethane, by reducing with sulphurous acid and precipitating with silver nitrate. If the periodide is dissolved, or merely suspended in ether and titrated with a standard solution of sodium thiosulphate, it will be found that of the *six* atoms of iodine only *five* can be titrated. This fact is very important, because it definitely proves that of the several atoms of iodine present in the molecule there is *one* that has an entirely distinct function, and this function corresponds to that of the bromine in triphenylbrommethane. Here again the titration must therefore be represented by the following equations:

$$2(C_6H_5)_3CI.I_5 + 10Na_2S_2O_3 = 2(C_6H_5)_3CI + 10NaI + 5Na_2S_4O_6.$$

$$(C_6H_5)_3CI + H_2O = (C_6H_5)_3C.OH + HI.$$

A few of the many analyses made will be given here.

0.5470 gram substance gave 0.7655 gram AgI.

0.5450 gram substance gave 0.3592 gram iodine by titration.

0.8805 gram substance gave 0.5788 gram iodine by titration.

0.4855 gram substance gave 0.6755 gram AgI.

0.7340 gram substance gave 0.4754 gram iodine by titration.

0.7700 gram substance gave 1.0650 grams AgI.

0.5680 gram substance gave 0.3651 gram iodine by titration.

	Calculated for $(C_6H_5)_3CI_5$.	Found. I.		II.	
Total iodine.....	75.79	75.65	....	75.18	75.10
Titrated iodine....	63.36	65.91	65.74	64.77	64.40

The carbinol formed in the reduction was identified by the melting-point, crystalline form, and by elementary analysis as such. Estimations of the yield of the carbinol gave results very close to those required by the equation.

It will be noticed from the figures of analysis that in all instances the titrated iodine was a little too high. This was puzzling, especially in view of the fact that the total halogen was always a little too low. The cause of this discrepancy was finally discovered to lie in the disturbing influence of the ether which is added in the titration. When either of the periodides is titrated with thiosulphate there is produced, at the early stages of the titration, triphenylbrommethane or triphenyliodomethane, and these form a coating over the crystals of the periodide; the further

action of the thiosulphate is in this way hindered. For this reason ether or some other solvent was added to keep the reduction products in solution. Triphenylbrommethane is affected by cold water only slowly, while the iodide is rapidly hydrolyzed, giving rise to the triphenylcarbinol and hydriodic acid. It is a well-known fact that in presence of certain substances hydriodic acid is far more affected by light than when pure. Pinnow[1] recently showed that small quantities of quinine and acridine sulphate exert a very appreciable effect upon the rate of oxidation of hydriodic acid solutions in water on exposure to light. I find that ether, also, greatly accelerates the oxidation. 50 cc. of a 0.5 per cent. solution of hydriodic acid, to which 15 cc. of ether were added, were exposed to ordinary diffused daylight for five minutes; almost 15 mg. of iodine were liberated in that short time. It is due, no doubt, to this influence of the ether present during the titration that high results are obtained in the case of triphenyliodo-periodide, while in the titration of the periodide of the brom-compound, ether has but little effect, as the solution remains nearly neutral till the end of the operation. Other immiscible solvents, such as chloroform, carbon disulphide, etc., also exert a marked influence upon the rate of oxidation. It seems therefore quite probable that the cause of this influence lies in the greater solubility of the iodine in the organic solvent than in water. The equilibrium being thus disturbed, more hydriodic acid will be oxidized.

Reactions of the Two Periodides. (1) *With Water.*—In this respect the two periodides behave absolutely alike. It has already been mentioned that during titration with sodium thiosulphate the triphenylcarbinol is formed. The same result can be reached without the use of any reducing agent, simply by boiling the periodides with water. Reduction of the iodides with a dilute solution of sulphurous acid, as described under the estimation of the total halogen, gave especially good results, the carbinol in both instances being formed quantitatively, and requiring no further purification. The carbinol was identified by its characteristic crystalline form and its melting-point (161°-162° C.) as well as by elementary analysis. There can be no doubt that in so far as the reaction with water is concerned the two periodides show exactly the same behavior.

[1] *Ber. d. chem. Ges.*, **34**, 2528.

(2) *Reaction with Alcohols.*—When triphenylbrom- or triphenyliodoperiodide is boiled with alcohol, and the excess of the iodine liberated in the reaction is removed by means of a solution of potassium iodide in water, the residue is triphenylmethane.[1] This formation of the hydrocarbon is not a result of the action of alcohol alone, but is caused by the hydriodic acid resulting from the interaction of the iodine and alcohol. This was established first, by a blank experiment with hydriodic acid and triphenylbrommethane; and second, by the following experiment, formed on each of the two periodides separately: The periodide was suspended in absolute alcohol, and to the solution small amounts of zinc dust were added, with constant stirring, until all the iodine was taken up by the zinc and the solution became clear. Water was now added, and the precipitated carbinol ether was freed from the alcohol and zinc iodide by filtration, and dried. The residue was recrystallized from ether and was identified as absolutely pure ethyl ether of triphenylcarbinol, $(C_6H_5)_3COC_2H_5$. No other products but the one mentioned were found. That the function of the zinc is no other than that of removing the "periodine" is quite evident from the fact that equally good results were obtained by substituting molecular silver for zinc. The action of alcohol upon the two periodides is therefore the same:

$$(C_6H_5)_3CBrI_5 + 5Ag + C_2H_5OH = (C_6H_5)_3COC_2H_5 + HBr + 5AgI.$$

$$(C_6H_5)_3CII_5 + 5Ag + C_2H_5OH = (C_6H_5)_3OC_2H_5 + HI + 5AgI.$$

In order to more positively insure the identity of the carbinol ethers an attempt was made to convert them into the acetyl derivative. According to Allen and Kölliker[2] the carbinol ether reacts with acetyl chloride as follows:

$$(C_6H_5)_3C.OC_2H_5 + CH_3CO.Cl = (C_6H_5)_3COC_2H_3O + C_2H_5Cl.$$

They give figures of analysis of the substance described by them as the acetyl derivative, and also found the melting-point to be at 99° C.

The carbinol ethers obtained by me from the periodides were subjected to the action of acetyl chloride. They dissolved in acetyl chloride with an evolution of heat, but there was no ethyl chloride

[1] This Journal, **22**, 768.

[2] *Ann. Chem.* (Liebig), **227**, 117.

given off. On cooling, white crystals separated. These were recrystallized from petroleum ether, and the substance was obtained in snow-white, perfectly transparent prisms. The melting-point, however, was found to be not at 99° C. but at 112° C. A closer examination of the substance established the fact that it was not at all the acetyl compound, but pure triphenylchlormethane. The discrepancy between the results of Allen and Kölliker and those which I have obtained are not due to the presence of some foreign substance in the carbinol ethers which were made from the periodides. A sample of the carbinol ether was made from absolutely pure triphenylchlormethane; it was recrystallized from alcohol and from petroleum ether, was absolutely free from halogen, and melted at 83° C., as given by Allen and Kölliker. 3.2 grams of this ether gave on treatment with acetyl chloride 2.90 grams of perfectly pure triphenylchlormethane, while the calculated quantity should have been 2.95 grams.

0.2446 gram substance gave 0.7312 gram CO_2 and 0.1268 gram H_2O.

0.5600 gram substance gave 0.2870 gram AgCl.

	Calculated for $(C_6H_5)_3C.Cl$.	Found.
Carbon	81.84	81.52
Hydrogen.....	5.44	5.76
Chlorine	12.75	12.66

It is evident that the action of acetyl chloride proceeds as follows:

$$(C_6H_5)_3C.OC_2H_5 + CH_3COCl = (C_6H_5)_3CCl + CH_3COOC_2H_5.$$

I also tested this action on the methyl and the propyl ethers of triphenylcarbinol, and found that they, too, give pure triphenylchlormethane.

This action of acetyl chloride is entirely analogous to that of the halogen acids. Silva[1] found that hydriodic acid decomposes mixed ethers, the halogen combining with that radical which contains the smaller number of carbon atoms. Lippert[2] confirmed this also for hydrochloric and hydrobromic acids on a large number of primary and secondary ethers. But the tertiary ethers, as was shown recently by Mammontoff,[3] behave in this respect differently. They, too, are readily decomposed by halogen acids, but

[1] *Ann chim. phys.*, [5], **7**, 429.
[2] *Ann. Chem.* (Liebig), **276**, 148.
[3] *Jour. Russ. phys. chim. soc.*, **29**, 236.

the halogen unites with the radical which contains the larger number of carbon atoms, as was shown by Mammontoff on the ethyl and propyl ethers of triphenylcarbinol,

$$(C_6H_5)_3C.OR + HX = (C_6H_5)_3C.X + R.OH.$$

The two reagents, hydrogen halide and acetyl halide, act therefore similarly upon triphenylcarbinol ethers.

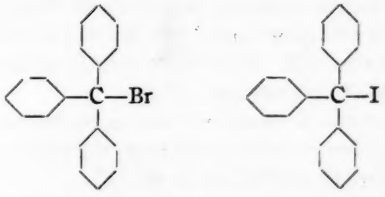
Whether the substance described by Allen and Kölliker was really the acetyl derivative or not, I cannot say. The low results which they got for hydrogen correspond better for triphenylchlormethane. An attempt will be made to prepare the acetyl derivative by some other method.

Methyl alcohol gave, with the periodides, the methyl ether of the carbinol melting at 82° C. With propyl alcohol the propyl ether was obtained.

(3). *Action of Metals.*—The action of metals upon the perhalides in neutral solvents such as ether, benzene, and acetic ester, results in the formation of the same unsaturated hydrocarbon, triphenylmethyl, which is produced when the normal halides are subjected to the same treatment. Of the different metals tried, zinc was found to give the most satisfactory results. Both periodides gave exactly the same results. The reaction is as follows:

$$(C_6H_5)_3CBrI_2 + 6zn = (C_6H_5)_3C + znBr + 5znI.$$
$$(C_6H_5)_3CI.I_2 + 6zn = (C_6H_5)_3C + 6znI.$$

From all that has been given in regard to the behavior of the two periodides we must conclude that the two react in every respect alike. Hence, they must not only have an analogous composition, but also a similar constitution. Consequently, the normal halides which gave rise to the perhalides must also have an analogous constitution:



5. TRIPHENYLIODOMETHANE.

In the first paper upon triphenylmethyl it was reported that tri-

phenyliodomethane was obtained. The yield of this product was, however, so small that only one analysis and a few qualitative tests were made. From 20 grams of triphenylchlormethane not more than 1 gram of the iodo-body was obtained. Although the reactions with ammonia and with the substituted amines, as well as the behavior of the periodide, showed conclusively that the substance produced by the addition of iodine to triphenylmethyl is the normal triphenyliodomethane, yet it appeared desirable to isolate the iodide itself in order to study its reactions directly. Of all the methods tried the following has given the best results: Triphenylmethyl is placed in a flask filled with dry carbon dioxide gas. A dilute solution of iodine in petroleum ether is added slowly to the hydrocarbon, the temperature of the flask being kept at about 60°-70° C. On cooling, there separates first a white crystalline substance, and later the iodide in clusters of large yellow prisms. The supernatant liquid is carefully decanted, the residue washed with petroleum ether, and dried in a stream of carbon dioxide. The crystals of the iodide can then be detached from the flask, and are at once put away in a closed bottle. I was able by this method to get 2.5 grams of the iodide from 2.3 grams of triphenylmethyl. The iodine was estimated by boiling the iodide with a dilute solution of sodium hydroxide containing a small amount of sulphurous acid, and precipitating the iodine in the filtered solution with silver nitrate.

I. 0.4620 gram substance gave 0.2982 gram AgI.

II. 0.5040 gram substance gave 0.3240 gram AgI.

	Calculated for $(C_6H_5)_3CI$.	Found. I.	II.
Iodine	34.29	35.05	34.72

The iodide possesses a light yellow color, but on exposure to light it darkens rapidly. The color of the iodide can best be observed when the substance is placed under ether, as it is only sparingly soluble in that solvent. It is soluble in hot acetic ether, but only slightly in cold. It is quite soluble in benzene and in carbon disulphide. It melts at 132° C.[1]

With *water* it reacts exactly in the same manner as the triphenylchlor- and brommethane, and gives the carbinol. This was so pure that it melted as obtained at 161° C.

0.3443 gram substance gave 1.1003 grams CO_2 + 0.2027 gram H_2O.

[1] In my first paper the melting-point of the iodide was given as about 135° C.

	Calculated for $(C_6H_5)_3C.OH$.	Found.
Carbon	87.64	87.15
Hydrogen	6.21	6.53

With *alcohol,* on heating, it gives triphenylmethane, which, however, is due to secondary reactions, just as is the case with the periodide. But when treated with alcohol in the cold, and better still with the addition of a little molecular silver, it gives the ether of the carbinol, just like the chloride and bromide of triphenylmethane,

$$(C_6H_5)_3CI + HOC_2H_5 = (C_6H_5)_3COC_2H_5 + HI.$$

With *metals* the reaction is again perfectly similar to that of triphenylchlor- and brommethane: triphenylmethyl is formed, which, on exposure to air, gives the insoluble peroxide,

$$(C_6H_5)_3CI + Ag = (C_6H_5)_3C + AgI.$$

When in solution, the iodo-compound decomposes readily, with liberation of some free iodine. Its reaction with *oxygen* is especially interesting. When a solution of the iodide is allowed to come in contact with air, or when oxygen is passed through the solution, iodine is liberated at once, and combines with a portion of the undecomposed iodide, forming the insoluble periodide[1]; also triphenylmethyl peroxide is produced. The decomposition by oxygen is not, however, as smooth as indicated by the equation

$$12(C_6H_5)_3CI + 5O_2 = 2(C_6H_5)_3CI.I_5 + 5(C_6H_5)_3C{-}O{-}O{-}C(C_6H_5)_3,$$

but depends upon a number of circumstances, such as the nature of the solvent, whether the oxygen be dry or moist, etc. This susceptibility to the action of oxygen, no doubt, is one of the principal causes why previous attempts[2] to prepare this substance have failed.

It should be noticed that in the preparation of the iodo-compound there was also isolated a small amount of a substance which melts only a few degrees lower than the triphenylmethyl peroxide, namely at 177°-178° C., and which possesses almost exactly the same solubilities as the peroxide. There is, however, reason to

[1] The periodide comes down in exceptionally beautiful crystals, of green iridescence. Analyses point that it is more likely the tetraiodide, $(C_6H_5)_3CI.I_4$. Organic bases also give lower periodides when the iodine is not directly added, but formed slowly in the solution, as by the oxidation of hydriodic acid. So caffeine under these conditions gives the diiodide in contrast to the tetraiodide, which is ordinarily formed. This Journal, **18**, 1.

[2] *Jour. Russ. Phys. and Chem. Soc.*, **29**, 238.

believe that it is not the peroxide, but a decomposition product of the iodide, because it was obtained in certain reactions in which the pure iodide was employed. The small quantity available did not suffice for a complete identification of this body.

Action of Silver Chloride.—When a solution of triphenylbrommethane in benzene is shaken for several days with silver chloride, dried at 200° C., it is completely converted into triphenylchlormethane. As the bromide can be obtained very pure this method of converting it into the chloride offers one of the best methods for getting the latter absolutely pure, when it is desired for physical constants. The conversion of the iodide into the chloride is not as smooth as that of the bromide. The reaction is necessarily slow because of the practically complete insolubility of silver chloride in benzene. The longer the time of the reaction the more of the triphenyliodomethane becomes decomposed in various other ways. The chloride of silver must be as finely divided as possible. It was prepared by precipitating it in water in the usual manner, washing the precipitate successively with alcohol, absolute ether, and benzene. It was kept under benzene until needed for the reaction. 2.5 grams of triphenyliodomethane gave about 1 gram of the crude chloride. It was necessary to recrystallize the latter several times in order to free it from the accompanying decomposition products of the iodide. Individual crystals could be picked out which possessed the crystalline form, the solubilities, and the melting-point of triphenylchlormethane.

0.4410 gram substance gave 0.1867 gram AgCl.

	Calculated for $(C_6H_5)_3C.Cl$.	Found.
Chlorine	12.75	10.45

6. FORMATION OF DOUBLE SALTS.

It was already mentioned that when zinc is allowed to act upon triphenylchlormethane the zinc chloride formed in this reaction unites with a portion of the still unreduced triphenylchlormethane. This combination is a heavy oil, perfectly insoluble in benzene, only very slightly in ether, and readily in acetic ester. The compound is something in the nature of a double salt. It can also be prepared by adding a solution of zinc chloride in ether to a solution of triphenylchlormethane in any solvent. All attempts to induce the oil to crystallize have proved fruitless. This tendency

on the part of triphenylchlormethane to enter into combination with salts of metals is by no means limited to zinc chloride. A compound of this nature with aluminum chloride was described by Norris.[1] The halide salts of mercury, tin, and antimony also give such combinations. Nor is it triphenylchlormethane alone that enters with metals into these peculiar combinations. It seems to be a property apparently common to all the phenylhalogenmethanes. These compounds are quite easily formed by triphenylbrommethane, tritolylchlormethane, diphenyldichlormethane, diphenylbrommethane, and in some instances even benzotrichloride gives rise to such derivatives. There can hardly be any doubt that this forms a general reaction which is shared not only by all phenylated halogenmethanes, but will be found to belong to analogous ethane and propane derivatives. In accordance with this I find that triphenyliodomethane also gives combinations with a great many salts of metals.

Why these halogenmethanes should at all give these combinations, is a question which requires further study. We are accustomed to think that usually substances themselves basic in nature form double salts with metals. But here we have a set of bodies which are supposedly non-basic; on the contrary, they share more the properties of acyl chlorides, and yet, they behave as salts of basic radicals. It is remarkable, that all these bodies possess intense color, from yellow to dark red, irrespective of whether the metal itself is colored or not. When first formed they are oils, but on scratching or cooling, most of them change to the crystalline form. Water and alcohol decompose these salts; they can be prepared, therefore, only in such solvents as ether, benzene, carbon disulphide, etc.

Benzotrichloride gives with *antimonic chloride* an orange-red precipitate. As this is formed even in absence of benzene it cannot be due to a previous condensation of the trichloride to triphenylchlormethane.

Benzophenone Chloride, $(C_6H_5)_2C.Cl_2$, forms dark red crystalline compounds, both with antimonic chloride and with stannic chloride.

Diphenylbrommethane, $(C_6H_5)_2CHBr$, gives similar salts with

[1] *Am. Chem. J.*, **23**, 54.

the above-mentioned reagents. They have not been analyzed.

The compound of *triphenylchlormethane* with *zinc chloride* could not be brought to crystallization. With *stannic chloride,* however, it is easily obtained in beautiful crystals on the addition of a benzene solution of the metal salt to one of triphenylchlormethane. The composition of this substance is identical with the one recently described by Kehrmann.[1]

0.2535 gram substance gave 0.3364 gram AgCl.

	Calculated for $(C_6H_5)_3C.Cl + SnCl_4$.	Found.
Chlorine	32.96	32.78

With *antimonic chloride,* the formation of the double salt is almost instantaneous, the precipitate consisting of fine red crystals.

0.7103 gram substance gave 0.2264 gram Sb_2S_5.

0.3261 gram substance gave 0.4785 gram AgCl.

	Calculated for $(C_6H_5)_3C.Cl + SbCl_5$.	Found.
Antimony	20.84	19.12
Chlorine	36.94	36.30

Crystalline salts were also obtained from triphenylchlormethane and *mercuric chloride,* and from *triphenylbrommethane* and *mercuric bromide.*

Tritolylchlormethane possesses, to an unusual degree, the tendency to combine with halogen salts of metals. The number of compounds which can be so obtained, is limited only by the number of salts of metals which can be brought into solution in some inert organic solvent. The salts are all intensely colored, finely crystalline, and are easily obtained exceptionally pure. The following few were analyzed.

With *zinc chloride* in acetic ester, orange-red crystals were obtained.

0.5108 gram substance gave 0.0920 gram ZnO.

0.4283 gram substance gave 0.4038 gram AgCl.

	Calculated for $(C_6H_4CH_3)_3C.Cl + ZnCl_2$.	Found.
Zinc	14.31	14.47
Chlorine	23.31	23.29

With *ferric chloride,* in dry ether, the double salt was precipitated in dark yellow, long needles.

0.3300 gram substance gave 0.7720 gram Fe_2O_3 and 0.2065 gram tritolylcarbinol.

[1] *Ber. d. chem. Ges.,* **34,** 3818.

	Calculated for $(C_6H_4CH_3)_3C.Cl + FeCl_3$.	Found.
Iron	11.74	12.13
Carbinol	63.10	62.60

Mercuric chloride, in acetic ester, gives a beautiful, bright red double salt.

0.3060 gram substance gave 0.1205 gram HgS and 0.1552 gram carbinol.

	Calculated for $(C_6H_4CH_3)_3C.Cl.HgCl_2$.	Found.
Mercury	33.84	33.88
Carbinol	50.86	50.82

Triphenyliodomethane shares with the halogenmethanes this peculiar property of entering into combinations with metals. It, too, gives a series of such bodies, but in many instances the formation of the double salt is accompanied by a partial oxidation of the iodo-compound. In most instances the formation of the salts was shown only in a qualitative way, leaving, however, no room for doubt that the iodide is in this respect, as in all others, entirely analogous to triphenylbrom- and triphenylchlormethane.

Stannic chloride, even in very dilute solutions, gives a dark red crystalline precipitate.

Antimonic chloride, for the most part, decomposes the iodo-compound, with liberation of iodine.

Zinc chloride and bromide give double salts which remain as oils, but with *zinc iodide* the salt becomes crystalline on scratching the oil. It is of a dark red, almost black, color.

SUMMARY.

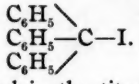
The experimental work detailed in this paper can now be summarized as follows:

Triphenylchlormethane and triphenylbrommethane.	The iodo-compound formed on the addition of iodine to the unsaturated hydrocarbon.
1. Empirical composition: $C_{19}H_{15}Cl, C_{19}H_{15}Br$.	1. $C_{19}H_{15}I$.
2. React with water readily and give triphenyl carbinol. With alcohol the ether is formed. With silver chloride the bromide gives triphenylchlormethane.	2. Reacts with water and with alcohol, and gives the same products as the bromide and the chloride. With silver chloride, triphenylchlormethane is formed.
3. With ammonia the amine, $(C_6H_5)_3CNH_2$, is produced.	3. Gives with ammonia the same amine, almost quantitatively.

4. React with substituted amines and give the corresponding bases $(C_6H_5)_3CNHR$.	4. Gives with amines also the same substituted bases; in some cases quantitatively.
5. The bromide gives rise to a perbromide and also to a periodide $(C_6H_5)_3CBr.Br_5$: $(C_6H_5)_3CBr.I_5$.	5. Forms with iodine, with about the same yield, a similar pentiodide, $(C_6H_5)_3CI.I_5$.
6. When acted upon by metals the chloride and the bromide give an unsaturated hydrocarbon, which, on exposure to air, forms triphenylmethyl peroxide, $(C_6H_5)_3C-O-O-C(C_6H_5)_3$.	6. Exactly the same unsaturated hydrocarbon is produced by the action of metals upon the iodo-compound.
7. Both unite with halides of metals, forming combinations of the nature of double salts.	7. Forms similar double salts.

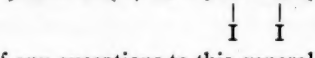
The facts described fully justify, I believe, the following conclusions:

1. The iodo-compound is triphenyliodomethane, and its constitution must be entirely analogous to that of the corresponding bromide and chloride,



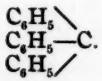
2. All the iodine added in the titration of the hydrocarbon is used up in the formation of this iodomethane; in other words, all the iodine is taken up by *one carbon atom.*

If these facts are to be interpreted in terms of the valence theory it must be admitted, that in case the hydrocarbon here described is really unsaturated, then we are dealing with a case of unsaturation which is entirely distinct in its nature from what is generally designated by this term. The unsaturation of one carbon atom in a molecule always implies a simultaneous unsaturation of another atom in the same molecule. In case of a hydrocarbon this second atom must, evidently, also be a carbon atom. We are accustomed to represent graphically such a state of unsaturation by a "double linking". In becoming saturated, as by the addition of halogens, each of the two atoms performs a similar function, each taking up one atom of halogen:



I am not aware of any exceptions to this general rule. But in the case of the unsaturated hydrocarbon under consideration *all* the

iodine, as I have shown, goes to *one* carbon atom. Hence, in the language of the valence theory, the unsaturation must be limited in this instance to one carbon atom in the molecule. The hydrocarbon must therefore, from this point of view, be represented by the constitution



The numerous facts which have been known for a long time, and which can be looked upon as supporting this view, were cited in the first paper[1] upon trivalent carbon. In a paper of recent date Thiele[2] expresses the opinion, that apart from the facts cited by me the existence of triphenylmethyl is no less supported by his theory of conjugated linkings and partial valencies. According to Thiele, we have here a case wherein the fourth valence of a methyl carbon atom is affected by the residual affinities of three phenyl carbon atoms. Such a neutralization of a valence of one carbon atom by three residual affinities of three other atoms is equivalent to a certain extent in its effect to what we have in Thiele's "conjugated system of double bonds", a stability not ordinarily present in unsaturated compounds. It will be noticed that this explanation involves a distribution of one valence of an atom in a certain indefinite way to several other atoms,—a theory not unlike Baeyer's "centric" theory of the constitution of benzene.

We may then arrange the derivatives of the hydrocarbon in a series, in order of increasing stability, something like this:

1. The unsaturated hydrocarbon, $(C_6H_5)_3C$.

2. Its ester and ether derivatives, obtained from 1. They, too, act as unsaturated.

3. Triphenyliodomethane, $(C_6H_5)_3CI$, can be obtained from 1 and 2.

4. Triphenylmethyl peroxide, $(C_6H_5)_3COOC(C_6H_5)_3$, is obtained from 1, 2, and 3.

We see that iodine can displace ethers and esters, and that oxygen can displace even iodine. The question comes up, is not the unsaturation of the hydrocarbon merely apparent unsaturation? Perhaps, we have here a case similar to Curtius' diazoacetic ester

[1] This Journal, **22**, 770.

[2] *Ann. Chem.* (Liebig), **319**, 124.

or to Pechmann's diazomethane. Both these substances absorb iodine[1] even in dilute solutions; in fact, they can be titrated by means of this reagent, the halogen replacing quantitatively the azo group. Perhaps the unsaturated hydrocarbon here described has the composition $(C_6H_5)_3C—R$, and this group R is being simply replaced by iodine, like the azo group in the two examples mentioned. If we assume that the R has a molecular weight equal to about one-fourth of that of triphenylmethyl, then we have an explanation why the unsaturated-like hydrocarbon takes up only four-fifths of the amount of iodine calculated for triphenylmethyl.

Against this view there are, it seems to me, a number of very valid reasons. In the first place, not taking into consideration unsaturated substances like fumaric and maleic acids, which take up no iodine at all in an alcoholic solution, there are a number of unsaturated bodies, others than triphenylmethyl, which absorb only from 10 to 80 per cent. of the calculated amount of iodine. Thus, crotonic and cinnamic acids absorb only about 8 per cent., styracine about 43, and allyl alcohol 85 per cent.[2] In the second place, by a series of experiments with different metals and with a variety of solvents, it was established that the fourth radical, if there be any, cannot come from the solvent. Thirdly, as will be shown in a paper soon to be published, this radical cannot come from the partial decomposition of triphenylchlormethane either. Strictly quantitative experiments on samples of 20 grams of triphenylchlormethane proved that the hydrocarbon can be obtained in yields of from 85 to 90 per cent. of the calculated amount.

Taking all these facts into consideration it seems to me that the constitution of the usaturated hydrocarbon is best represented as $(C_6H_5)_3C$.

Further study of the hydrocarbon itself as well as of its behavior towards different oxygen and nitrogen derivatives is in progress.

To Mr. M. Hanson, who assisted me in the prosecution of this work, I desire to express my thanks.

ANN ARBOR, MICHIGAN,
April, 1902.

[1] *J. prakt. Chem.*, **38**, 422; *Ber. d. chem. Ges.*, **27**, 1889.
[2] Lewkowitsch: "Chemical Analysis of Oils and Fats," p. 176.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 64.]

THE AMMONIUM TUNGSTATES.[1]

BY THOMAS M. TAYLOR.

Received March 12, 1902.

THE two general classes of ammonium tungstates are designated paratungstates and metatungstates. Laurent[2] first proposed the name paratungstates, giving to these salts the formula $5M_2O.12WO_3.nH_2O$, which was confirmed by Marignac[3] who also presented numerous other types. The metatungstates were first prepared by Margueritte,[4] but their name was suggested by Laurent. Later Scheibler and Marignac studied them and arranged them under the general formula $M_2O.4WO_3.nH_2O$. From the numerous formulas proposed for the type members, these seem best established, and the salts used in the present study conformed to them.

SOLUBILITY OF AMMONIUM PARATUNGSTATE.

$(NH_4)_{10}W_{12}O_{41}.11H_2O$.

The solubility of the "para salt," as given by different chemists, is as follows:

Investigator.	Ratio of salt to water.	Temperature.
Anthony	1 : 25–28	"Cold"
Lotz	1 : 26.1	10.7°
Lotz	1 : 33.3	"Cold"
Lotz	1 : 5.8–9.6	100°
Marignac	1 : 22–38	15°–18°
Taylor	1 : 59.3	26°
Taylor	1 : 69.8	21°
Taylor	1 : 74	21°
Taylor	1 : 52.7	29°

SOLUBILITY OF AMMONIUM METATUNGSTATE.

Lotz	1 : 0.84	15°
Riche	1 : 0.35	"Ordinary"

These discrepancies are irritating. When ammonia is passed into water containing tungstic acid, a white substance remains which has been called "paratungstate," but which is remarkably insoluble. It is far more insoluble than any ammonium paratungstate met with in the present investigation.

[1] From the author's thesis presented for the Ph.D. degree, 1901.

[2] *Ann. chim. phys.* [3], **21**, 54 (1847).

[3] *Ibid.* [3], **69**, 24 (1863).

[4] *Ibid.* [3], **17**, 475 (1846).

AMMONIUM PARATUNGSTATE.

$(NH_4)_{10}W_{12}O_{41}.11H_2O$.

When a solution of "para salt" is evaporated at slightly elevated temperature, monoclinic needles crystallize out; when evaporated at a boiling temperature, flat plates appear. These needles have been described as orthorhombic prisms by Kerndt, Schabus and Marignac. Examined microscopically in polarized light they show an apparent parallel extinction, and give a biaxial interference figure, with the acute bisectrix parallel to the long axis of the crystal, and therefore appear to be orthorhombic, but give these orthorhombic reactions on account of their remarkable twinning structure, which closely resembles the wedge-shaped penetration figures seen in the hydrated zeolites,—more particularly stilbite, which is orthorhombic in form but is a complicated monoclinic twin. It is an interesting fact that these ammoniated and hydrated crystals exhibit the same internal structure as the hydrated zeolites.

Crops of crystals usually consist of mixtures of needles and plates in varying proportion; many previous analyses have undoubtedly been made with such material. Such a mixture, consisting largely of needles, was digested for three days in forty times its weight of water. The water was removed and the same amount added and allowed to stand again for three days. The needles remaining contained no admixed plates. This separation does not prove that the plates are the more soluble, for they are smaller and would therefore dissolve out first. But whatever the reason for this separation, the purpose in view was accomplished: the needles were isolated. These on analysis gave the following data:

Tungsten trioxide, determined by ignition in a porcelain crucible:

"Para needles." Grams.	WO_3. Grams.	WO_3. Per cent.
4.0016	3.4395	85.95
3.1344	2.6938	85.94

The ammonia was determined by the usual distillation and titration method.

"Para needles." Grams.	NH_3. Gram.	NH_3. Per cent.
2.9265	0.15370	5.25
2.1002	0.10983	5.23

The water was determined as follows: The salt was covered with lead oxide, and ignited in a combustion tube in a current of dry air; the water and ammonia were caught in sulphuric acid and weighed. Subtracting from this weight that of the ammonia, the weight of the water was obtained.

"Para needles." Grams.	$NH_3 + H_2O$. Gram.	Water. Per cent.
1.2458	0.1813	9.31
1.0636	0.1536	9.20
1.5988	0.2262	8.91

These values correspond to the formula $(NH_4)_{10}W_{12}O_{41}.11H_2O$, which requires WO_3, 85.87 per cent.; NH_3, 5.24 per cent.; H_2O, 8.88 per cent.; and are also a confirmation of Marignac's formula.

When the "para needles" are crystallized from boiling water, monoclinic plates separate (extinction parallel to diagonal of rhombic section, axial plane lying in the plane of symmetry), and to obtain these with no admixed needles, it is necessary to keep the water at the boiling-point, and to remove the plates from the boiling solution as fast as they are formed. Some plates prepared in this way, gave on ignition the following per cent. of tungsten trioxide:

"Para plates." Gram.	WO_3. Gram.	WO_3. Per cent.
0.6931	0.6170	89.02
0.2528	0.2249	88.96
0.3216	0.2816	88.93
0.5905	0.5253	88.96

The theoretical requirement of tungsten trioxide for $(NH_4)_{10}W_{12}O_{41}.5H_2O$, is 88.83 per cent. and this also confirms Marignac's formula. On comparison, these two para salts show as follows:

"Para needles." $(NH_4)_{10}W_{12}O_{41}.11H_2O$.

"Para plates." $(NH_4)_{10}W_{12}O_{41}.5H_2O$.

Thus it would appear that the "para needles" in boiling water, lose 6 molecules of water.

AMMONIUM METATUNGSTATE.

$$(NH_4)_2W_4O_{13}.8H_2O.$$

Margueritte[1] first prepared this salt by boiling the para salts with tungstic acid. Laurent[2] prepared it, by the continued boiling of the aqueous solution of the para salts. Scheibler[3] made it by heating the para salt to 250°, until ammonia was given off, causing

[1] *Ann. chim. phys.* [3], **17**, 475 (1846).
[2] *Ibid.* [3], **21**, 62 (1847).
[3] *J. prakt. Chem.*, **83**, 304 (1861).

a partial separation of tungstic acid, then dissolving the residue in water and allowing it to crystallize. This method was adopted by Persoz[1] and later by Marignac[2].

Scheibler describes the salt as crystallizing in large tetragonal octahedra, which effloresce in the air. If the crystals have been scratched or bruised, they quickly lose water and become opaque. Marignac observed that the crystals lose 7 molecules of water at 100°, and the remaining molecule is not driven out below 200°. Riche noticed the same behavior. When alcohol is added to a hot solution of the "meta salt", the salt $(NH_4)_2W_4O_{13}.6H_2O$ separates, and, according to Marignac, loses 5 molecules of water at 100°.

In the present investigation the "meta salt" was prepared by boiling an aqueous solution of the "para salt" for two or three days, evaporating to small bulk and allowing the syrupy liquid thus obtained to stand. Large transparent tetragonal octahedra were obtained. After three or four recrystallizations, the crystals became almost colorless, but the yellow tint was difficult to remove. Boiled with purified bone-black the greater part of the original brown color may be removed. The crystals have a high index of refraction, which is true also of their solution. These crystals of "meta salt" were also prepared by heating the "para needles" at 150°, for four hours.

On analysis the salt gave 3.05 per cent. of ammonia.

"Meta salt." Gram.	NH_3. Gram.	NH_3. Per cent.
0.5016	0.01531	3.05

This corresponds to $(NH_4)_2W_4O_{13}.8H_2O$, which contains 3.02 per cent. of ammonia, confirming Scheibler's formula. The characteristic physical properties were in such accord with the published data that further analysis was not undertaken.

COLLOIDAL AMMONIUM TUNGSTATE.

$(NH_4)_2W_6O_{19}.4$ or $6H_2O$.

On repeating the method of Scheibler to obtain the "meta salt" (*i. e.*, heating the "para needles" to 250°), a colloidal "gum" was obtained. As many as twenty experiments failed to substantiate his claims, for the "meta salt" was produced at 150°. This "gum" would dry hard, become transparent and had a high index of re-

[1] *Ann. chim. phys.* [4], **1**, 101 (1864).
[2] *Ibid.* [4], **3**, 72 (1864).

fraction. It did not cement itself to porcelain, in the way "colloidal tungstic acid" is said to do, but would shrink away from the sides of the containing vessel, and could easily be removed. Under the microscope "para needles" were found embedded in it, and were removed by dialysis. The fraction passing through the parchment paper in a few hours, crystallized in tetragonal octahedra; later fractions in "para needles," and still later fractions would not crystallize at all but consisted largely of "gum" which had passed through. This "gum" therefore, when first prepared, consists of a mixture of "para salt," "meta salt," and a "colloidal salt."

The best condition for getting a large yield of the "gum" is as follows: Pulverized "para needles" are spread out on a watch-glass, and heated in an air-bath at 220° for one hour. The air-bath must allow the escape of water and ammonia. The product is covered with water and boiled vigorously for fifteen or twenty minutes, when a clear, but dark, heavy liquid results. This is filtered away from any residue and on evaporation dries into the "gum" with an almost quantitative yield. On standing several days in water, the residue will pass into the "gum" without previous boiling. At higher temperatures considerable tungstic acid is separated and the yield is not so good. The "meta" salt free from "para" must be heated to 250°, before yielding the "gum," and the yields are nothing like so large, as when the "para salts" are taken for the starting-out material.

A marked darkening of the original white salt is noticed after heating. Different fractions of the "para salts" yield the "gum" with different degrees of readiness. These facts point to the presence of some impurity which may affect the transformations.

After dialyzing a portion of the "gum" for six days it gave the following analysis:

"Gum." Gram.	WO_3. Gram.	WO_3. Per cent.
0.6150	0.5447	88.57
"Gum." Grams.	**NH_3. Gram.**	**NH_3. Per cent.**
0.4825	0.01279	2.65
1.3776	0.03848	2.79

Another sample was dialyzed for thirteen days, through parchment paper, using ten changes of water of 2½ liters each. The dialyzer had a diameter of 15 cm. After four or five days, the increase of volume in the inner vessel ceased. The resulting col-

loidal salt, when dried on the water-bath and allowed to stand in the air, slowly increased in weight. When dried at the ordinary temperature and allowed to stand, it decreased in weight. A portion of the "colloidal salt," dried on the water-bath, gave the following analysis:

"Colloidal salt." Gram.	WO_3. Gram.	WO_3. Per cent.
0.4469	0.4089	91.49
0.4523	0.4143	91.60
"Colloidal salt." Gram.	NH_3. Gram.	NH_3. Per cent.
0.6334	0.01520	2.40
0.5985	0.01415	2.36

These results point to the formula $(NH_4)_2W_6O_{19}.4H_2O$, which requires ammonia 2.24 per cent. and tungsten trioxide 91.82 per cent.

In the same way another portion of "gum" was dialyzed for fourteen days, using nearly double the amount of water previously used (twelve changes of water of 3½ liters each). The resulting "colloidal salt" dried at the ordinary temperature gave the following analysis:

"Colloidal salt." Gram.	WO_3. Gram.	WO_3. Per cent.
0.1227	0.1101	89.73
0.2100	0.1885	89.76
"Colloidal salt." Grams.	NH_3. Gram.	NH_3. Per cent.
0.9243	0.01996	2.16
1.0301	0.02184	2.12

These percentages are close to the formula $(NH_4)_2W_6O_{19}.6H_2O$, which requires ammonia 2.29 per cent., and tungsten trioxide 89.69 per cent. This sample was dried at the ordinary temperature, the previous one at 100°. Since the salt loses weight on standing, it is likely that the additional water does not represent such a definite number of molecules as these analyses would indicate.

To compare the percentage of ammonia, in the different salts, the following table is given:

Salt.	NH_3. Per cent.
"Para needles"	5.24
"Para plates"	5.42
"Meta salt"	3.02
"Colloidal salt" (dialyzed six days)	2.72
" " (" thirteen days)	2.38
" " (" fourteen days)	2.14

The dialyzed salt dries hard and clear like glass, with a yellowish tint, contains no embedded crystals, and under no conditions could it be made to crystallize. It has a high index of refraction and is miscible with water in nearly all proportions. It may prove of value as a mounting medium in microscopic work, and also for the mechanical separation of minerals.

Its solution has an acid reaction and absorbs ammonia with avidity. One long series of dialyzations was spoiled, by working with ammonia in the same room, the "colloidal salt" changing to the "meta" and "para" salts. By treating the solution of the "colloidal salt" with tenth-normal ammonia, till the acidity is barely neutralized, it passes into the "meta salt". Unless care is used considerable amounts of the "para salts" will be formed.

Under certain conditions the "colloidal salt" passed into a white modification, which on microscopical examination proved to be an emulsion, the globules closely resembling fat globules. On drying, the white emulsion gradually passed into the transparent variety. The emulsion can be produced by cooling a clear concentrated solution with ice-water. Frequently a more dilute solution, would be filled with spurious clouds, floating in suspension, which appeared to be some foreign matter. This could not be filtered out and was a source of annoyance, until it was examined microscopically, and found to be the emulsion. Emulsions are common enough among organic substances, but are rarely observed with inorganic salts.

At first it was thought that this "colloidal salt" might be "colloidal tungstic acid," but since after prolonged dialysis, the ammonia could not be removed, it was taken to be a colloidal ammonium tungstate.

The history of "colloidal tungstic acid" is of some interest. Graham,[1] in 1864, reported the existence of "colloidal tungstic acid," which he prepared by treating a 5 per cent. sodium paratungstate solution with dilute hydrochloric acid and dialyzing the mixture. The resulting heavy liquid had such a high specific gravity, that glass would float on it. Sabanejeff[2] made a molecular weight determination using cryoscopic methods, and reported the formula $3WO_3.H_2O$. Later[3] he retracted his determinations,

[1] *Proc. Roy. Soc.*, London, **13**, 340 (1864).
[2] *J. Russ. Chem. Soc.*, **21**, 1 (1889).
[3] *Ztschr. anorg. Chem.*, **14**, 354 (1897).

and published an article on the "Non-Existence of Colloidal Tungstic Acid," saying that he had previously taken Graham's word for the composition of the "gum." On examination he found it was impossible to dialyze out the sodium, and concluded that it was amorphous sodium metatungstate. His proof of this is open to criticism, for: he states that the salt had a marked acid reaction; his analyses do not conform closely to the theoretical for sodium metatungstate; and the periods of dialysis used were not long enough to thoroughly separate the material. The conversion of one form into the other was rather violent. Sabanejeff changed the amorphous salt into the crystallized variety, by heating to 130°-150°, in a sealed tube with an excess of water. This temperature is about the same as that which changes the ammonium "para salt" to the "meta salt" and seems altogether too high to prove the dimorphism, of the two sodium salts. Had the acidity of his colloidal salt been gradually neutralized with sodium bicarbonate or carbonate, the salt might have reverted to the crystallized form, and its dimorphism thus been disproved. It seems probable that his dimorphous colloidal sodium metatungstate may prove to be a colloidal sodium tungstate analogous to the colloidal ammonium tungstate prepared in the present investigation.

TEMPERATURE AT WHICH THE AMMONIUM SALTS BEGIN TO LOSE AMMONIA.

Some "para needles" were placed in a glass U-tube immersed in an oil-bath and dry air was rapidly passed over them into Nessler's solution. It was found that if the glass tube leading into the solution, was etched on the inner surface, a brown ring would form on the roughened surface, several minutes before the solution showed any traces of color. The moment of formation of this brown ring, was taken as the signal for the first appearance of ammonia, and the temperature of the bath noted. In this manner the "para needles" began to lose ammonia at 60°. The "para plates" at the same temperature, and the "meta salt" at 120°.

It is significant that the "meta salt" should begin to lose ammonia at 120° as it was prepared at 150°. It seems improbable that a salt which begins to lose ammonia at 120° could be made at 250°, as recorded by Scheibler.

Marignac and others dry the "para salts" at 100° and attribute the loss to expulsion of water, but a part of that loss is ammonia.

However, the ammonia that escapes below 100° is but a trace.

ACTION OF DRY AMMONIA GAS ON "PARA NEEDLES."

The effect of ammonia on "para needles" was determined as follows: A boat, filled with needles, was placed in a bent tube immersed in paraffin. Ammonia gas (dried by lime and caustic potash) was passed over it, and escaped through 0.75 cm. mercury and 9.00 cm. of water, so that the gas was under a pressure of about 14 mm. of mercury, in excess of the atmospheric pressure. After heating for one and a half hours the boat was placed in a capsule and weighed. The percentage of ammonia was then determined. The loss in weight, together with the percentage of ammonia furnish data, from which the changes in the salt may be calculated.

ACTION OF DRY AMMONIA GAS ON AMMONIUM PARATUNGSTATE.

Temperature.	"Para needles." Grams.	Weight after treatment.	NH_3. Gram.	Molecules of NH_3 added.	Molecules of water lost.	Approximate formula.
		Original "para needles."				$10NH_3.12WO_3.16H_2O$
100°	0.7193	0.6904	0.04276	+1.3	— 8.5	$11NH_3.12WO_3.7H_2O$
110°	1.0012	0.9632	0.06295	+2.0	— 8.7	$12NH_3.12WO_3.7H_2O$
120°	1.1203	1.0796	0.07268	+2.4	— 8.8	$12NH_3.12WO_3.7H_2O$
130°	0.9936	0.9619	0.06901	+3.2	— 8.8	$13NH_3.12WO_3.7H_2O$
140°	0.8391	0.8101	0.05563	+2.7	— 8.7	$13NH_3.12WO_3.7H_2O$
150°	1.2278	1.1768	0.07514	+1.7	— 9.1	$12NH_3.12WO_3.7H_2O$
160°	1.2204	1.1696	0.06530	+0.2	— 7.7	$10NH_3.12WO_3.8H_2O$
200°	0.9730	0.9251	0.04797	—0.6	— 8.3	$9NH_3.12WO_3.8H_2O$
250°	1.3238	1.2286	0.05872	—1.6	—11.5	$8NH_3.12WO_3.4H_2O$

Attention is directed to the nearly constant loss of water; and that at 130° the maximum amount of ammonia is absorbed. Tungsten trioxide was separated at 250°.

These ammonia-addition salts are quite unstable; when dissolved in water, the water is made alkaline and "para needles" crystallize out; when allowed to stand in the air they revert to their original weight, and percentage of ammonia, as evidenced in the following experiments: Two boats containing "para needles" placed side by side in the same U-tube were heated together in dry ammonia gas at 130° for one and a half hours. The ammonia in one was determined at once; the companion boat was allowed to stand over night, before determining the ammonia.

	"Para needles." Gram.	NH_3. Gram.	NH_3. Per cent.
Boat A.	0.8754	0.06242	7.13
Companion Boat A.	0.9718	0.05034	5.18
Boat B.	0.8744	0.05859	6.70
Companion Boat B.	0.9321	0.04866	5.22

Companion Boat B, after standing over night, weighed 0.9319 gram. It appears therefore that the salt has lost its added ammonia, and absorbed its lost water.

ACTION OF MOIST AMMONIA GAS ON THE "META SALT" AT THE ORDINARY TEMPERATURE.

A boat containing 0.9874 gram of "meta salt" was placed in a vacuum desiccator, over ammonium hydroxide. After standing several hours, the transparent crystals were found to be replaced by a white salt covered with water. This water was removed by spontaneous evaporation in the air, and the residue weighed 0.9327 gram and contained 0.04803 gram ammonia, equivalent to 5.15 per cent., or 3.83 molecules of ammonia added. Hence the "meta salt" has been changed by moist ammonia gas, at the ordinary temperature into the "para needles," and the conversion has been practically quantitative.

The "para needles" being a hundred times more insoluble than the "meta salt," have crystallized out from the water of crystallization of the latter. In other words the water of the old salt has been pushed out by the new salt, and the new salt is found "swimming" in the water of crystallization of the old salt. After standing several days the amount of water in the boat gradually increased, so that water evidently slowly distils into the boat.

ACTION OF MOIST AMMONIA GAS ON THE "META SALT" AT 100°.

"Meta salt" treated with ammonia passes to the "para needles;" the latter in solution change at 100° to the "para plates" so that the action of moist ammonia on the "meta salt" at 100° can almost be predicted. A boat containing 0.4408 gram of "meta salt" (placed in the same apparatus used for determining the action of dry ammonia on the "para needles") was treated with moist ammonia gas at 100°, for one hour. After treatment, the salt weighed 0.4189 gram; after standing sixty hours in the air it weighed 0.4186 gram. This contained 0.02276 gram of ammonia equivalent to 5.44 per cent., or 4.04 molecules of added ammonia.

Hence at 100° moist ammonia gas transforms the "meta salt" into the "para plates." Dry ammonia gas would probably form the ammonia-addition product produced at that temperature.

THEORETICAL CONSIDERATIONS.

NORMAL AMMONIUM TUNGSTATE.

The normal sulpho-salt $(NH)_2WS_4$ exists and one might expect the existence of the corresponding oxygen salt. However, normal ammonium tungstate has never been prepared. Marignac,[1] by the spontaneous evaporation of a solution of "para salt," in a bell-jar over lime (which would absorb water and not ammonia), obtained a salt of the composition $2(NH_4)_2O.3WO_3.3H_2O$. This salt was soluble in cold water but soon changed to the "para salt." In the air it gave off ammonia reverting to the "para salt."

The ratio between the ammonia and tungsten trioxide, in the different salts is tabulated as follows:

Salt.	NH_3.	:	WO_3.
Theoretical normal salt	1.0	:	0.5
Marignac salt (unstable)	1.0	:	0.75
"Meta salt"	1.0	:	2.0
"Para salt"	1.0	:	1.2

It is seen from these ratios that Marignac's salt approaches more closely to the normal ratio than any salt which has yet been prepared, but it was not stable at the ordinary temperature. Of the other salts, the "para salt" follows next in order.

The para ammonio-addition salts prepared in this investigation are unstable, easily losing their excess of ammonia. It seems therefore that at the ordinary temperature, tungsten can not hold any more ammonia than that expressed by the para ratio. It is believed that the formation and preservation of the normal salt is simply a question of temperature.

WATER OF CRYSTALLIZATION.

In boiling water the "para needles" lose exactly 6 molecules of water and crystallize out as "para plates." Five molecules of water remain in the salt, and it is significant that 5 ammonium oxide molecules remain also. Possibly 5 ammonium oxide molecules influence 5 water molecules in such a manner, that the latter are more firmly bound or linked than the others. Whatever ex-

[1] *Ann. chim. phys.* [3], **69**, 22 (1863).

planation may be advanced, the fact remains that 6 molecules of water are driven out at 100°, and 5 are not.

The "meta salt" $(NH_4)_2W_4O_{13}.8H_2O$ at 100° loses 7 molecules of water. The remaining molecule can not be driven out below 200°. The "meta salt" from alcohol, $(NH_4)_2W_4O_{13}.6H_2O$, loses at 100° 5 molecules of water, and the remaining molecule behaves as before. In these salts 1 molecule of water must be very differently combined from the others, for one requires 200° of temperature to remove it, while the others leave the salt quite rapidly even at the ordinary temperature. The number of water molecules remaining again correspond to the number of ammonium oxide molecules, and the probability increases that 1 ammonium oxide molecule influences 1 hydrogen oxide molecule.

These two salts may be written:

$$[2NH_4OH.4WO_3].[7H_2O]$$
$$[2NH_4OH.4WO_3].[5H_2O]$$

At 100° in the air the water is split off from both salts, and the common residue or nucleus $[2NH_4OH.4WO_3]$ remains, which is stable at 200°.

AMMONIA CONTENT.

The "para needles" and "plates" begin to lose ammonia at 60°; the "meta salt" at 120°. If the ammonia in these salts is combined in the same manner, it ought to be given off at the same temperature. Such is not the case, and consequently it looks as though part of the ammonia was combined or linked differently from the rest. At 150° the "para salts" lose 4 molecules of ammonia, and revert to the "meta salt." The "meta salt" on the addition of 4 molecules of ammonia advances to the "para salt." The commonest double salt of sodium with ammonium paratungstate, has the composition $Na_4(NH_4)_6W_{12}O_{41}.15H_2O$ (Knorre, Marignac, Hallopeau). Four molecules of ammonia have been replaced by 4 molecules of sodium. The fact that all the ammonia has not been displaced by sodium, indicates that 4 molecules are differently combined than the others, and probably these are the same 4 which are lost at 150° (or on long standing in water, even at the ordinary temperature).

TRANSFORMATIONS.

The transformations in this series of salts are of interest. The

entire series may be prepared from the first member or the entire series may be prepared from the last member. In fact, the whole series may be prepared from any member.

Temperature of formation.	Series.	
(Below 100°)	"Para needles"	$(NH_4)_{10}W_{12}O_{41}$. $11H_2O$
(100°)	"Para plates"	$(NH_4)_{10}W_{12}O_{41}$. $5H_2O$
(150°)	"Meta salt"	$(NH_4)_2W_4O_{13}$. $8H_2O$
(220°)	"Colloidal salt"	$(NH_4)_2W_6O_{19}$. 4 or $6H_2O$

Before taking up the transformations, attention may be called to the difference between the last two salts. This difference is $2WO_3.2$ or $4H_2O$. Gibbs[1], in his classic work on the complex inorganic acids, pointed out the existence of a "homologous series" of metatungstates having a common difference $2WO_3.RO$. The difference noticed here, while not exactly the common difference discovered by him, is equivalent to it, as far as the tungsten trioxide is concerned.

The two "para salts" (in the series) on long standing in solution, at the ordinary temperature revert to the "meta salt." The "colloidal salt," on absorbing ammonia, reverts to the "meta salt." The "meta salt" on standing reverts to the residue [$2NH_4OH.4WO_3$]. This residue, therefore, may be considered a decomposition product or nucleus of the whole series. It is the most stable portion in the entire series; when it is attacked, the structure of the salt is broken down, and tungstic acid separates. It is well known that the "meta salts" are broken down by acids or alkalies only with difficulty.

Beginning with the first member, we may go down the series by physical means: "Para needles" heated to 100° (in water) go into the "para plates." The "plates" at 150° (in air) pass into the "meta salt." The latter heated to 250° changes to the "colloidal salt."

Again we may proceed down the series by chemical means. "Para needles" treated with acetic acid go to the "para plates."[2] The "para plates" boiled with tungstic acid or dilute mineral acids pass into the "meta salt." The "meta salt" as yet has not been changed into the "colloidal salt" by chemical means; boiling with tungstic acid did not produce it.

[1] *Proc. A. A. A. S.*, **47**, 1 (1898), and previous papers.

[2] Gibbs: *Am. Chem. J.*, **1**, 229 (1879). Gibbs states that the salt formed with acetic acid has the composition $(NH_4)_{10}W_{12}O_{41}.6H_2O$, and adds that it appears to be the same salt, to which Marignac attributed $5H_2O$. The temperature of crystallization may clear up the discrepancy.

To reverse the transformations: Beginning with the last member we may proceed up the series by chemical means. The acidity of the "colloidal salt" neutralized with ammonia, produces the "meta salt." The "meta salt" on the addition of 4 molecules of ammonia at 100° advances to the "para plates." The "para plates" on the addition of water at the ordinary temperature proceed to the "para needles."

From these considerations it appears probable that a common nucleus runs through the whole series, and that the nucleus is $[2NH_4OH.4WO_3]$. The molecular weight of this nucleus is as yet unknown; it may be a polymer, or it may be one-half, which would correspond to Gibbs' difference $[RO.2WO_3]$, and might be written

$$\begin{matrix} NH_4 \\ H \end{matrix} > O.2WO_3.$$

The simplest view of the matter would favor the nucleus $[NH_4OH.2WO_3]$, and until molecular weight determinations have been made, the salts may be written with this in mind.

AMMONIUM "PARA" AND "META" TUNGSTATES.

Temperature of formation.		
(Below 100°)	"Para needles"	$6[NH_4OH.2WO_3].4[NH_4OH].6[H_2O]$
(100°)	"Para plates"	$6[NH_4OH.2WO_3].4[NH_4OH]$
(150°)	"Meta salt"	$2[NH_4OH.2WO_3].7[H_2O]$
(220°)	"Colloidal salt"	$2[NH_4OH.2WO_3].2[WO_3].3$ or $5[H_2O]$

PARA-AMMONIO-ADDITION-PRODUCTS.

In ammonia gas.	
(100°)	$6[NH_4OH.2WO_3].\ [NH_4OH].4[NH_3]$
(110°)	$6[NH_4OH.2WO_3].\ [NH_4OH].5[NH_3]$
(120°)	$6[NH_4OH.2WO_3].\ [NH_4OH].5[NH_3]$
(130°)	$6[NH_4OH.2WO_3].\ [NH_4OH].6[NH_3]$
(140°)	$6[NH_4OH.2WO_3].\ [NH_4OH].6[NH_3]$
(150°)	$6[NH_4OH.2WO_3].\ [NH_4OH].5[NH_3]$
(160°)	$6[NH_4OH.2WO_3].2[NH_4OH].2[NH_3]$
(200°)	$6[NH_4OH.2WO_3].2[NH_4OH].\ [NH_3]$
(250°)	$4[NH_4OH.2WO_3].4[WO_3]\ \ .4[NH_3]$

PARA-AMMONIO-SUBSTITUTION SALT.

(Below 100°)	$6[NH_4OH.2WO_3].4[NaOH].10[H_2O]$

These tables suggest the presence of "nuclei" and "side-chains," The "para salts" appear to be polymers of the "meta salts," linked together by, or to which are added, the "side-chains." The "side-chains" may be split off by physical or chemical means, and

substitutions appear to take place in them. Where transformations require the splitting off of part of the structure, both physical and chemical means may be employed to accomplish the desired end. But where transformations demand the addition of these parts, then chemical means only can accomplish the purpose.

Smith[1] and Hardin have demonstrated the tendency of tungsten trioxide itself to polymerize. And after such polymerization the material is insoluble in sulphur monochloride, whereas before, it is soluble. The polymerized ammonium salts in this series are over a hundred times more insoluble than the unpolymerized.

It is significant that the temperature which breaks down the "para salt" into the "meta salt" (*i. e.*, 150°) is not far from that temperature (130°) at which the "para salt" in ammonia gas is able to take on the maximum amount of ammonia. In other words, the polymer absorbs the most ammonia at a temperature near its rupture temperature. It looks as though the polymer when "opened up" was enabled to add more ammonia.

There is no reason why the compounds of carbon should have a monopoly over "homologous series," "polymerizations," "ring formations," "side-chains," "substitution products" or "gums."

Organic "gums" are supposed to be high polymers of some simple form, and the polymerization is usually accompanied with insolubility and non-crystalline character. The "gum" in the present investigation appears to be an ammonium salt, but no surprise will be expressed if it proves to be an acid salt of "colloidal tungstic acid" and ammonium metatungstate. If "colloidal tungstic acid" exists, it would probably be a polymer of tungsten trioxide and its affinity for ammonia would be so great that only with difficulty could the two be separated. In one experiment, a long process of dialyzation was ruined by the presence of ammonia in the atmosphere of the room, and who knows how much ammonia the other experiments absorbed? Traces of ammonia would neutralize the work performed by days of dialyzation. The subject needs to be further investigated.

It is hoped that benzylamine tungstate will form a similar series of salts, and, yielding more readily to organic methods, facts concerning their molecular magnitude and constitution may be developed.

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[1] This Journal, **21**, 1007 (1899).

THE APPLICATION OF ESCHKA'S METHOD TO PIG IRONS.

By John V. R. Stehman.

Received April 11, 1902.

Of the three methods generally used for the determination of sulphur in pig iron,—the evolution method, the oxidation method in the wet way, and Bamber's method,—it is generally known that at least two of them are not always accurate.

The evolution method does not, for some irons, give accurate results. The amount of sulphur evolved as hydrogen sulphide plus that remaining unacted on in the residue is less than the amount obtained by either the oxidation or Bamber's method. This error is especially noticeable in those irons containing a high percentage of combined carbon.

The oxidation in the wet way does not, with some irons, effect the complete oxidation of the sulphur, a portion of it remaining with the residue of graphite and silica. Bamber's method is generally used when the oxidation method does not effect its purpose, and no doubt is the safest, besides doing away with the precipitation of the sulphur by barium chloride from a concentrated solution of ferric chloride. When a platinum dish is available, it affords a simple method.

The thought occurred to the writer that if it were possible to reduce the sample of pig iron to a fine powder, its oxidation might be effected in the presence of a basic mixture, such a mixture for example as magnesia and sodium or potassium carbonates. The sulphur, it was hoped, would be converted into soluble sulphates of the bases present, and any small quantity of sulphides of these metals formed could be oxidized by bromine, as in the determination of sulphur in coke. The writer has been informed that v. Reis[1] has already applied this modified Eschka method to pig irons, but his paper is not accessible to me.

Two mixtures were made as follows: One of magnesia 2 parts and sodium carbonate 1 part, well ground and mixed, and another of magnesia 4 parts, potassium carbonate 1 part and sodium carbonate 1 part. The addition of potassium carbonate, it was thought, would hasten the oxidation, potassium carbonate having a slight solvent action on ferric oxide. It was first thought that the samples of pig irons had to be ground very fine, and to accom-

[1] Stahl und Eisen, 8, 827.

plish this the agate mortar was used, with the result that with a great deal of labor a small sample was finally obtained. Upon treating this sample of about 1 gram with the mixture of magnesium oxide and sodium carbonate, in a platinum crucible at a full red heat, it was found that oxidation was rapid, about fifteen minutes being required to effect it. After a little experimenting it was found that samples of 80 and 60 mesh were oxidized completely, while samples of 30 mesh were not. In fact 50 mesh seemed to be the limit of coarseness of sample.

The samples of basic pig irons as delivered to this laboratory have been crushed in a steel mortar, a pestle and hammer being used. The operation requires about five minutes for a 20-gram sample of 60 mesh. This is done because we wish to have a sample that has been treated under as nearly as possible the same conditions as our basic pig irons. A sample so treated, quite frequently cannot be drilled.

For carrying out the experiments herein described, four samples of gray irons were thus prepared of 80 and 60 mesh each. A given quantity of each iron was all ground to pass through an 80-mesh seive and a 60-mesh sample was prepared in the same way.

No. 1. Gray forge pig iron: Si, 1.22; S (?).

No. 2. Chilled basic pig iron: Si, 0.55; S (?).

No. 3. Sample C of the American Foundrymen's Association: Si, 1.783; S, 0.076.

No. 4. Sample B of same: Si, 1.076; S, 0.056.

The following method was finally decided upon: 3 grams of the sample of a fineness higher than 50 mesh are weighed into a platinum crucible of 30 cc. capacity and 3 grams of the basic mixture are added. The greater part of this mixture is added at once and the whole thoroughly mixed. The balance, about 0.5 gram, is used in covering the top of the mixture. The crucible is then placed over a Bunsen flame, a shield being used to prevent the products of combustion of the flame from coming in contact with the mixture. A description of this shield will be given later. The part of crucible exposed to the flame is heated for one hour at a full red heat. At the end of this time the mass will be found sintered together, and can be broken up when cold with a glass rod, extracted with hot water into a No. 2 beaker, and 10 cc. of bromine water added. It is best to always add a fixed amount as bromine frequently contains sulphur, and by using the

same amount in a blank determination this error will be eliminated. The solution is boiled for fifteen minutes on the hot plate and filtered, taking care to see that the filtrate is perfectly clear. The residue is washed with hot water, and to the filtrate 1.5 cc. of concentrated hydrochloric acid are added. The bromine is expelled by boiling, and sulphur is precipitated in the boiling solution by 10 cc. of a hot 10 per cent. solution of barium chloride.

The products of combustion of the gas must be kept away from the contents of the crucible. This can be done without the use of a shield if care is used, at least when gasoline is used for furnishing gas.

It was decided to treat samples Nos. 1 and 2 by each of the following methods:

First. Evolution Method.—Absorption of hydrogen sulphide in solution of potassium hydroxide, oxidation of the potassium sulphide formed by potassium permanganate solution, acidifying with hydrochloric acid, clearing with oxalic acid, neutralizing with ammonia, making slightly acid with hydrochloric acid and precipitation of the sulphur as usual. The sulphur in the residue is determined and added to that obtained as hydrogen sulphide, 10 grams of the sample being used.

Second. Oxidation in the wet way by solution in concentrated nitric acid with the addition of 3 grams of potassium chlorate when solution is complete, and the usual evaporation and resolution with the final precipitation of the sulphur in the 100 cc. solution, using a hot saturated solution of barium chloride and having the ferric chloride solution just short of boiling. The sulphur is determined after standing twelve hours.

Third. Bamber's method as described by Blair, third edition.

SAMPLE NO. 1.

Evolution method + S in residue.	HNO_3 and $KClO_3$.	Bamber's method.	Oxidation in presence of basic mixture.	Time used in igniting.	Fineness of sample.	Mixture used.		Shield.
0.035	0.036	0.035	0.039	1.5 hr.	80 mesh.	MgO & Na_2CO_3.		No
0.036	0.035	0.036	0.039	1.5 hr.	"	"	"	No
0.036	0.035	0.034	0.040	1 hr.	"	"	"	No
0.035	....	0.035	0.042	1 hr.	"	"	"	No
....	....	0.036	....	....	....	....	....	....
Average:								
0.035	0.035	0.035	0.040	....	....	....	....	....

It was thought that the increase of sulphur as shown by this method was due to the flame, the basic mixture absorbing sulphur therefrom. To prevent this an asbestos board 8 inches by 4 inches was used; in the center of this board and near the lower edge a clean hole was cut, of a size sufficient to admit the crucible for about seven-eighths of its length, and forming a snug fit. To the upper edge of this board was hinged, by means of a copper wire, a board of the same length but 3 inches wide and without any hole. The whole arrangement represents an "A" tent affair, open at both ends, which can be placed over the tripod in such a manner that when the crucible is put into place about seven-eighths of its length projects through the board and rests upon the platinum triangle. The products of combustion from gas pass off above and away from the crucible.

The results obtained on sample No. 1, using the shield, were as follows:

SAMPLE NO. 1.

Nos.	Oxidation in presence of basic mixture.	Fineness of sample.	Time of ignition.	Mixture used.
1	0.0399	60 mesh	$1\frac{1}{2}$ hours	MgO, K_2CO_3 & Na_2CO_3
2	0.0394	"	1 hour	" "
3	0.0385	"	1 "	" "

No. 3 was evaporated to dryness after expelling bromine, redissolved in water slightly acid with hydrochloric acid, and filtered, the sulphur being determined in the filtrate. This, at least, shows that the higher results obtained on this sample were not due to any sulphur absorption from the flame. The use of potassium carbonate shows no decided gain in action or time.

To test the efficiency of the shield, several blank determinations were made with, and without, its use, and the following results obtained.

Three grams of the basic mixture were used and the ignition continued for one hour.

Nos.	Without shield.	With shield.
1	0.0025 gram $BaSO_4$ found	0.0025 gram $BaSO_4$ found
2	0.0024 " " "	0.0025 " " "
3	0.0025 " " "	0.0024 " " "
4	0.0026 " " "	0.0023 " " "

There is evidently no decided advantage in the use of the shield when gasoline gas is used, and care is exercised in igniting the mixture, the flame being kept away from the front or mouth of

the crucible. No. 4 of the above, without shield, was ignited so that the flame partly passed by the mouth of the crucible.

The writer is not able to state the value of the shield when ordinary gas is used, but at all events an alcohol lamp of good-sized flame may be safely used.

SAMPLE NO. 2.

Evolution + residue.	HNO_3 and $KClO_3$.	Bamber's method.	Oxidation in presence of basic mixture.	Time of ignition.	Fineness of sample.	Mixture used.		Shield.
0.032	0.032	0.030	0.031	1 hour	60 mesh	MgO, K_2CO_3 & Na_2CO_3		No
0.032	0.030	0.031	0.031	45 min.	"	"	"	Yes
0.032	0.030	....	0.032	1 hour	"	"	"	Yes
....	0.032	....	....	....	....	....	....	....

The sulphur was precipitated directly without any previous evaporation to dryness.

In samples Nos. 3 and 4 the sulphur has been determined by the following: 1. Booth, Garrett and Blair; 2. Cramer and Bicknell; 3. Andrew S. McCreath; 4. Albert W. Smith. In the following table their respective numbers are placed after their results.

SAMPLE NO. 3.

Evolution + S in residue.	Chemist's number.	HNO_3 oxidation.	Chemist's number.	Bamber's method.	Chemist's number.	Oxidation in presence of basic mixture.	Fineness.	Time.	Shield.
0.066	1	0.075	2	0.076	1	0.077	60	1 hr.	Yes
....		0.075	3	....		0.076	60	1/2 hr.	No
....		0.076	4	....		0.076	60	1 hr.	No

SAMPLE NO. 4.

Evolution method + residue.	Chemist's number.	HNO_3 oxidation.	Chemist's number.	Bamber's method.	Chemist's number.	Oxidation in the presence of basic mixture.	Fineness.	Time.	Shield.
0.043	1	0.058	2	0.054	1	0.054	80	1 hr.	No
....		0.055	3	....		0.057	60	1 hr.	Yes
....		0.058	4	....		0.056	60	1 hr.	Yes
....		....		....		0.043[1]	30	1 hr.	Yes

[1] Results obtained with 30-mesh sample clearly show an incomplete oxidation.

The above samples have all been gray irons. White iron it was thought, on account of its low silicon and absence of graphitic carbon, would not lend itself as readily to oxidation; but samples of white irons, treated in the same way, were oxidized as completely and in the same time as gray.

SAMPLE OF WHITE IRON.

	Per cent. sulphur.	Per cent. sulphur.	Per cent. sulphur.
Bamber's method.....	0.431	0.432	0.429
Oxidation in basic mixture ...	0.432	0.430	0.430

This method could no doubt be worked to advantage, using a stream of oxygen and combustion tube. The method does away with the precipitation of the sulphur in the presence of the ferric salt, and the time required for a determination is about that required for the determination of sulphur in coke.

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THE CONSTITUTION OF CAMPHENE.[1]

BY F. D. DODGE.

Received April 17, 1902.

THE constitution of camphene is as yet an unsettled point in the chemistry of the terpene series. The objections to the Bredt formula[2] have been stated by Semmler[3] and others, but no satisfactory substitute has been suggested.

As a result of some experiments with the reaction of Bertram and Walbaum,[4] the addition of acetic acid, in presence of mineral acids, I have been led to a somewhat different conception of the camphene molecule.

Camphene and pinene yield the acetates of isoborneol and terpineol, respectively. As regards other terpenes, but little appears to have been published, and I have made the following experiments.

1. *Pinene*, from American turpentine (sp. gr. 0.867. $\alpha_D = +11°$). 50 cc. with 100 cc. pure acetic acid, containing 1 per cent. sulphuric acid, allowed to stand at 15°-20° for five days. Quantitative saponification showed 43 per cent. terpineol acetate.

[1] Read before the New York Section of the American Chemical Society, February 7, 1902.

[2] *Ber. d. chem. Ges.*, (1893), p. 3056.

[3] *Ibid.*, (1900), p. 3421.

[4] *J. prakt. Chem.*, **49**, 1.

2. *Camphene* (by Reychler's method from pinyl chloride), after six days, product contained 77 per cent. isobornyl acetate.

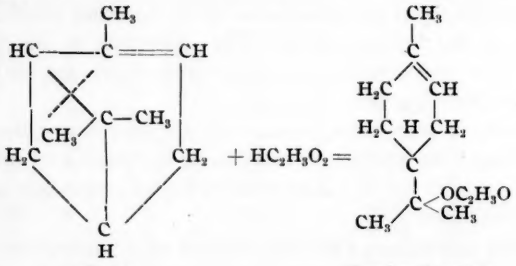
3. *Limonene* ($\alpha_D = +100°$. Sp. gr. $= 0.847$), after five days, $\alpha_D = 0°$, product showed 4 per cent. of acetate. On distillation, about 50 per cent. of a terpene mixture was obtained, containing principally terpinene.

4. *Terpinolene* (from terpineol by oxalic acid), after six days, 11 per cent. acetate formed.

5. *Terpinene* (from limonene), after six days, 8 per cent. acetate.

It is to be noted that the bornylene of Wagner, to which must probably be assigned the camphene formula of Bredt, also does not combine with acetic acid under these conditions, which fact was utilized by Wagner to separate it from camphene.[1]

Pinene and camphene are thus sharply differentiated from the other terpenes. The acetic reaction is not obtained (or but to a limited extent) with any singly or doubly unsaturated terpene, except in the case of pinene. But in pinene, the double bond is not attacked, but the 4-ring is opened, producing a terpineol derivative.



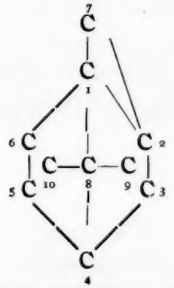
Pinene. Terpineol acetate.

The possibility now suggests itself, that in camphene we may have, not a double bond, but a 4-ring (or possibly a 3-ring) which is readily opened, yielding the ester of isoborneol.

The close relations of camphene, isoborneol, and camphor indicate with great probability that camphene contains the camphor nucleus, in which case there are but two possibilities of such additional ring-formation.

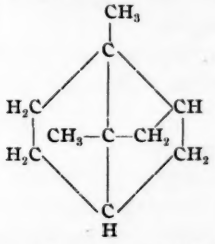
[1] *Ber. d. chem. Ges.*, (1900), p. 2121.

1. A 3-ring between C_1, C_2, and C_7.



A study of the spacial relations as shown by the tetrahedral models leads to the conclusion that such a structure is improbable. This assumption would also lead to a formula for camphenilone, which is identical with that established for the fenchocamphorone of Wallach.[1] These two compounds are, however, certainly not identical, and the C_1, C_2, C_7 ring hypothesis is hence untenable.

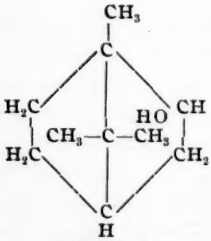
2. A 4-ring, C_1, C_2, C_9, C_8, leads to the formula



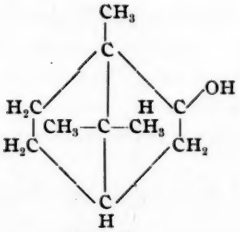
which, I believe, best explains the properties and reactions of camphene.

As in the case of pinene, we have here a 4-atom ring, readily opened under the influence of acids, yet differing from pinene in one respect. When the 4-ring of pinene is separated, the molecule is rearranged in more stable forms either of the terpineol or camphor series, and reversion to pinene is impossible. In camphene, the atoms composing the 4-ring are, as it were, held in position by the stable 5- and 6-ring nucleus, and the 4-ring may be opened and closed *ad libitum; i. e.,* we can pass from camphene to isoborneol, and the reverse at will. To isoborneol must be assigned the cis-configuration, while borneol is represented by the trans-form.

[1] *Ann. Chem.* (Liebig), **300**, 294; **302**, 371; **315**, 273.



Isoborneol.

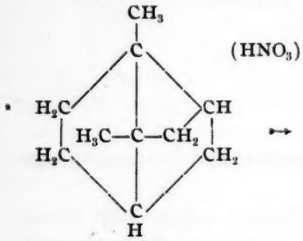


Borneol.

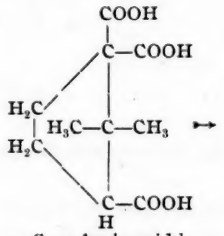
The greater reactivity of isoborneol is due to the proximity of the hydroxyl to the C_9 methyl group, and the differences in properties of the cis-chloride (isobornyl chloride, camphene hydrochloride) and the trans-chloride (bornyl chloride, pinyl chloride) are similarly explained.

According to this hypothesis, camphene is a saturated molecule, *i. e.*, contains no double bond. In fact there appears to be very little reason to consider it unsaturated. The difficult oxidation by permanganate, the action of bromine, etc., and many other reactions show that camphene is differently constituted from the typical unsaturated terpenes.

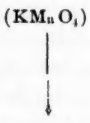
The new formula explains very satisfactorily the various oxidation products of camphene. Thus, we have:

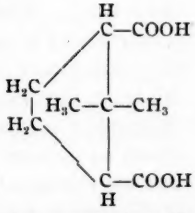


Camphene.



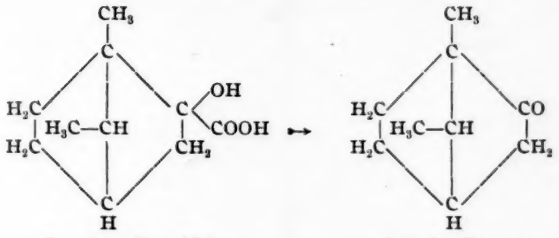
Camphoric acid.[1]





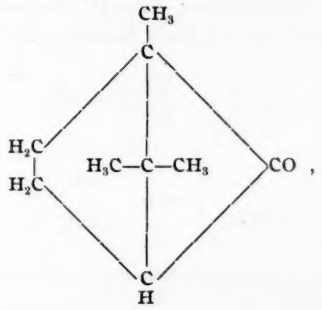
Apo-camphoric acid.

[1] *J. Chem. Soc.* (1891), p. 648.

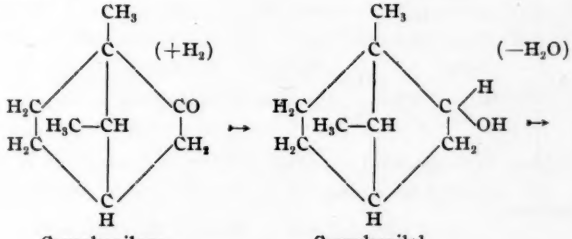


Camphenylic acid.[1] Camphenilone.

Camphenilone, $C_9H_{14}O$, here appears as a true lower homologue of camphor, which it strikingly resembles. Jagelki's formula,[2]

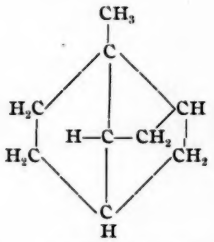


is improbable, because it assumes an oxidized 4-carbon ring, which is known to be an unstable arrangement, and it leads further to very improbable formulas for dehydrocamphenylic acid, and camphenilene. The new formula presents no serious difficulties. Thus:



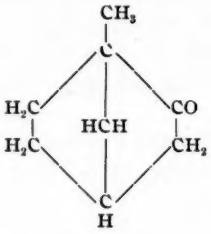
Camphenilone. Camphenilol.

[1] *Chem. Centrbl.*, (1897), I, p. 1056.
[2] *Ber. d. chem. Ges.*, (1899), p. 1498.

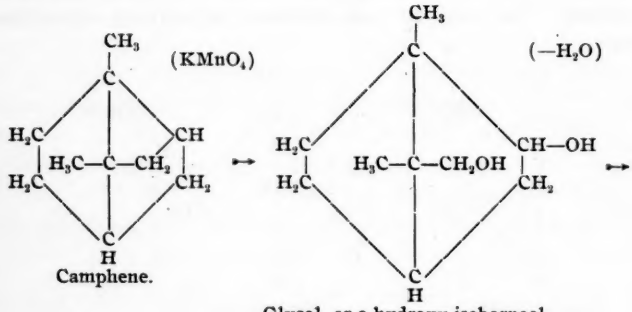


Camphenilene.

These reactions are exactly analogous to the formation of camphene from camphor, and if the hypothesis is correct, it should be possible to put camphenilene through further transformations, leading finally to the second lower homologue of camphor:

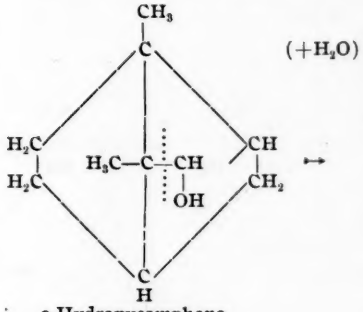


Wagner's camphene glycol[1] and its reactions may be shown as follows:

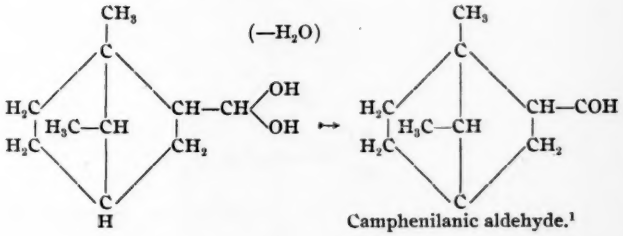


Camphene. Glycol, or 9-hydroxy-isoborneol.

[1] *Ber. d. chem. Ges.*, (1890), p. 2311.



9-Hydroxycamphene.



Camphenilanic aldehyde.[1]

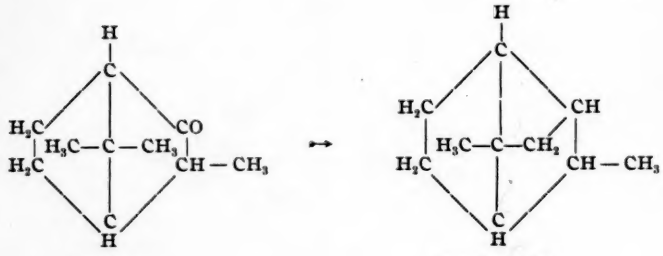
Further oxidation then leads to camphenilanic acid, camphenylic acid, and camphenilone.

As regards the other oxidation products mentioned by Jagelki (*l. c.*), it is unnecessary to discuss them in detail. Blaise,[2] who has examined and repeated some of Jagelki's work, arrives at rather different results. He concludes that the former's camphenilone formula cannot possibly be correct, and that this compound does not contain the trimethylcyclopentene ring characteristic of the camphor series. This deduction is entirely in harmony with the formulas here suggested.

A few other points in connection with the camphene formula remain to be mentioned.

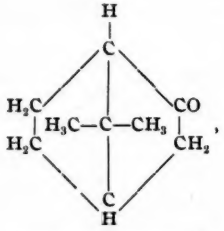
It has been shown[3] that fenchene behaves, with acetic acid, like camphene, and we are led to an analogous formula:

[1] *Chem. Ztg.*, (1896), p. 842. *Ber. d. chem. Ges.*, (1899), p. 1498.
[2] *Compt. rend.*, **129**, 886.
[3] Schimmel & Co.: *Chem. Centrbl.*, (1898) II., p. 985.



Fenchone. Fenchene (?).

But, fenchocamphorone has, most probably, the structure,



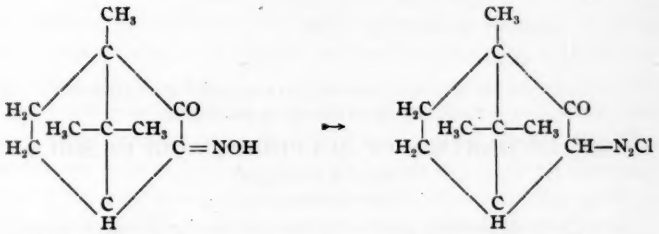
Fenchocamphorone.

and its formation from this fenchene is hard to explain. Wallach,[1] however, has recently shown that ordinary fenchene is a mixture of at least three compounds, and Kondakow and Lutschinin[2] have reached a similar conclusion. The conditions in the fenchone series appear to be complex, and further experiment is necessary.

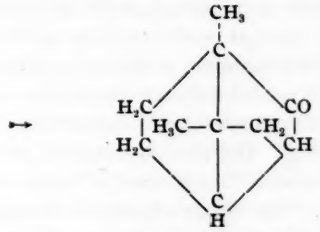
The characteristic feature of the new camphene formula is the connection between C_2 and C_9. Now the symmetry of the camphor nucleus shows that if such a connection is possible, a similar one may occur between C_3 and C_9.

In fact a compound is known, which I believe is best represented by such a formula. This is the camphenone of Angeli[3] whose formation may be shown thus:

[1] *Ann. Chem.* (Liebig), **302**, 371; **315**, 273.
[2] *Chem. Ztg.*, **25**, 131.
[3] *Gazz. chim. ital.*, **23**, (II.) 351; **24**, (II.) 318.

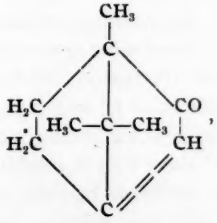


Isonitrosocamphor. Diazocamphor, HCl.



Camphenone (?).

Angeli proposed the formula



but the tetrahedral models show that this structure is highly improbable. Harries and Matfus[1] have further found that camphenone does not show the hydroxylamine reaction characteristic of $\alpha\beta$-unsaturated ketones.

I would add, finally, that camphenilone, if correctly formulated above, should yield isonitroso and oxy-methylene derivatives, which are improbable if Jagelki's formula is true. These reactions are under investigation.

NEW YORK, February, 1902.

[1] *Ber. d. chem. Ges.*, **32**, 1340.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

DETERMINATION OF SULPHURIC ACID IN SOILS.

BY C. B. WILLIAMS.

Received March 13, 1902.

SULPHUR generally occurs in the soil in the form of sulphates and has been heretofore estimated by slightly acidifying the soil solution with hydrochloric acid, boiling and then precipitating by slowly adding barium chloride with constant stirring. After standing a few hours, the precipitate is filtered, washed, dried and weighed as barium sulphate and calculated to sulphur trioxide.

There are three difficulties generally encountered in determining sulphuric acid in soils: (1) The small quantity of the constituent usually present; (2) the solubility of some of the barium sulphate precipitate in the ferric chloride or aluminum chloride or both, which are almost invariably present; (3) as well as on the other hand the strong liability of the precipitate becoming contaminated by iron, especially if the soil is of a ferruginous character and the soil solution is not strongly acid.

Lunge[1] found that in determining sulphur in pyrites unless the solution is strongly acidulated with hydrochloric acid, considerable iron is carried down with the barium sulphate and is not removed by washing; on the other hand he found that the barium sulphate is dissolved by the solution if too strongly acid. Experiments by Jannasch and Richards[2] show that if sulphuric acid is precipitated in the presence of iron, a double barium iron sulphate is formed which, when ignited, sets free sulphur trioxide. They, in the light of their work, stated that to obtain correct results the iron had to be removed before precipitation with barium chloride.

The conditions and difficulties cited above are similar to those that frequently obtain when we come to determine sulphur in soils, for not infrequently soils contain as much as 5 to 15 per cent of ferric oxide. Now if Lunge found it difficult to estimate sulphur with any degree of accuracy in the presence of iron in pyrites, then may we not expect to encounter difficulty when we attempt to estimate it in soils where the relative proportion of iron

[1] *Ztschr. anal. Chem.*, **19**, 419-431.

[2] *J. prakt. Chem.*, **39**, 321.

to sulphur is vastly greater and the sulphur usually in such minute quantities as to require the greatest precision without unfavorable conditions?

The writer in analyzing soils during the past year noticed that if iron and alumina were first removed by precipitation with ammonia, the results were considerably higher in almost all instances than if the acid was precipitated direct as directed in the methods prescribed by the Association of Official Agricultural Chemists. It was also observed that the precipitate was coarse-grained and did not tend to run through the filter as it did if precipitated in the presence of iron and alumina.

In the following table are recorded comparative results obtained by the two methods, or rather two modifications of the same method. Those under "official" are obtained by the method prescribed by the Association of Official Agricultural Chemists, while those under "modified" are results obtained by first removing the iron and alumina before precipitating the barium sulphate.

	Per cent. sulphur trioxide.		
Soil No.	Official method.	Modified method.	Difference.
58	0.013	0.040	0.027
59	0.019	0.037	0.018
60	0.022	0.034	0.012
61	0.015	0.036	0.021
62	0.012	0.031	0.019
63	0.039*	0.039	....
64	0.020	0.040	0.020
65	0.015	0.032	0.017
66	0.011	0.030	0.019
67	0.050	0.061	0.011
68	0.013	0.029	0.016
70	0.057	0.065	0.008
71	0.027	0.041	0.014
72	0.026	0.031	0.005
73	0.017	0.027	0.010
74	0.022	0.038	0.016
75	0.021	0.031	0.010
76	0.026	0.041	0.015
77	0.034*	0.034	....
78	0.110*	0.106	....
79	0.021*	0.031	....
80	0.103	0.123	0.020
81	0.087*	0.106	....
82	0.027	0.055	0.028
83	0.058*	0.050	....

* Barium sulphate colored brown by the presence of iron.

Soil No.	Per cent. sulphur trioxide. Official method.	Modified method.	Difference.
84	0.065	0.098	0.033
85	0.034	0.087	0.053
86	0.007	0.082	0.075
87	0.003	0.045	0.042
88	0.024	0.057	0.033
89	0.000	0.050	0.050
90	0.082	0.093	0.011
91	0.017	0.046	0.029
92	0.041	0.058	0.017
93	0.027	0.034	0.007

In the first eleven results by both methods, 4 grams of soil were taken for the determinations, in the next twelve, 2 grams for the "official" and 1 gram for the "modified," and in the last twelve 1 gram for the "official" and 2 grams for the "modified" methods. It is seen that the differences generally with the last twelve soils by the two methods are much greater than in the preceding twenty-three. The explanation for this greater divergence seems to lie in the amount of soil taken for analysis, as all other conditions were identical and it is noticed that when only 1 gram of soil is used with the "official" method the sulphuric acid is precipitated in such a finely divided condition that a little will pass the most retentive filter-paper (No. 589, S & S, blue ribbon) unobserved, unless the filtrate is examined very closely by transmitted light.

Whatever else may be said, the results in the table point very clearly to the fact that when sulphuric acid is precipitated in the presence of iron and alumina some of the barium sulphate is dissolved by either the ferric chloride or aluminum chloride or by both, and that it can only be determined accurately in soil solutions in which these two bases have been eliminated. If the results by the "modified" method are correct, and it can not be seen why they are not, as the ferric and aluminum hydroxides were in all instances washed at least ten times, using about 20 cc. at each washing, then the "official" method lacks over 35 per cent. of getting out all the sulphur trioxide in the above thirty-five samples.

In an experiment to test the solubility of barium sulphate in ferric chloride, it was found that when a solution was taken containing 0.110398 gram ferric chloride and 0.001288 gram of sulphuric acid (the averages of both sulphur trioxide and ferric chloride in the thirty-five samples experimented with when 2 grams of

soil are taken), that 17 per cent. of the sulphur trioxide was dissolved, results being obtained in closely agreeing duplicates. In a preliminary experiment it was observed that if the solution was only slightly acid (0.2 cc. excess of concentrated hydrochloric acid) iron in some form, probably an oxychloride, was frequently deposited on the bottom of the beaker in boiling prior to the addition of barium chloride, and stuck so tenaciously as to be removed only by the addition of considerably more hydrochloric acid. This same phenomenon was often observed in working with soils containing a moderately high percentage of iron with only a slight acidity of the soil solution.

In the experiment above to ascertain the solubility of barium sulphate in ferric chloride, 3 cc. excess of hydrochloric acid were present, as this was sufficient to prevent the deposition of iron and was found in a preliminary trial to exert an inappreciable, if any, dissolving effect.

Although the determination of sulphuric acid is not at present considered by soil chemists of the highest importance, because it generally exists in most soils in sufficient quantity for the complete development of crops for years to come, yet its importance as an essential constituent of plant food and its probable deficiency in many instances has prompted the writer to submit the above results and observations.

THE INTERACTION OF SULPHURETTED HYDROGEN AND ARSENIC ACID.[1]

By L. W. McCay.

Received March 31, 1902.

From solutions of arsenic acid which have been treated with sulphuretted hydrogen I have been able to separate large amounts of monosulphoxyarsenic acid in the form of its tertiary sodium salt, and small amounts of disulphoxyarsenic acid, also in the form of its tertiary sodium salt. In addition to the above-mentioned acids the solutions appear to contain some trisulphoxyarsenic acid. Thus far, however, all attempts to isolate this compound have failed. If we assume its existence in the solutions, and a number of facts warrant us in making the assumption, the action of

[1] The facts given in the first part of this article have been taken from a paper which appeared in the *Ztschr. anorg. Chem.*, **29**, 36 (1901).

sulphuretted hydrogen upon arsenic acid would appear to be in harmony with Ostwald's law of successive reactions (Gesetz der Reactionsstufen). The successive stages through which arsenic acid passes during its transformation into sulpharsenic acid would then find expression in the following equations:

I. The sulphuretted hydrogen is always present in large excess.

$$1.\ H_3AsO_4 + H_2S = H_3AsO_3S + H_2O$$
$$2.\ H_3AsO_3S + H_2S = H_3AsO_2S_2 + H_2O$$
$$3.\ H_3AsO_2S_2 + H_2S = H_3AsOS_3 + H_2O$$
$$4.\ H_3AsOS_3 + H_2S = H_3AsS_4 + H_2O$$

Since sulpharsenic acid cannot exist in the free state we have:

$$2H_3AsS_4 = As_2S_5 + 3H_2S.$$

The sulphoxyarsenic acids, however, are unstable compounds and when the sulphuretted hydrogen is present in the solutions in but small amounts they break down partially, the monosulphoxyarsenic acid into arsenious acid and sulphur, the disulphoxyarsenic acid into arsenious acid, sulphur and the sulphides of arsenic. The sulphuretted hydrogen then converts the arsenious acid into arsenic trisulphide. Some arsenic pentasulphide is also formed according to I. We'll have then:

II. The current of sulphuretted hydrogen is slow or intermittent, so that the gas is not continually in excess:

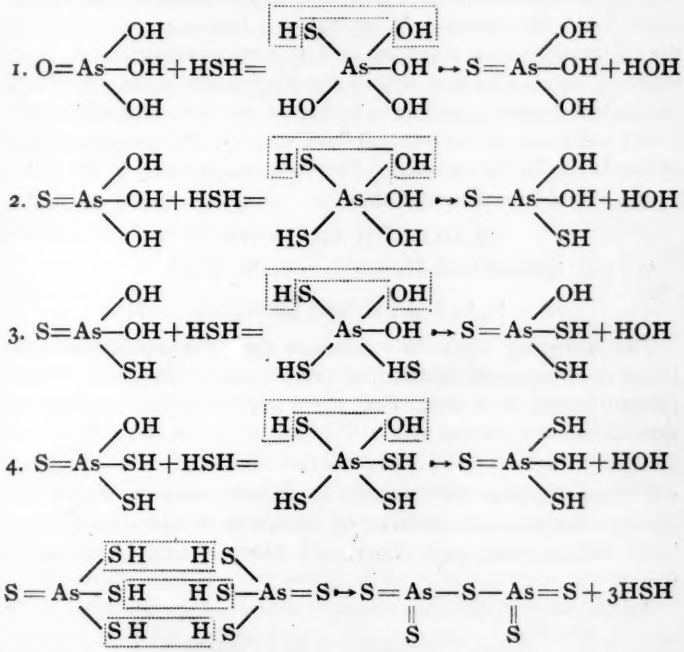
$$1.\quad H_3AsO_4 + H_2S = H_3AsO_3S + H_2O$$
$$2.\quad 2H_3AsO_3S = 2H_3AsO_3 + 2S$$
$$3.\quad 2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$$
$$4.\quad H_3AsO_3S + H_2S = H_3AsO_2S_2 + H_2O$$
$$5.\quad 6H_3AsO_2S_2 = As_2S_5 + As_2S_3 + 4S + 2H_3AsO_3 + 6H_2O$$
$$6.\quad 2H_3AsO_2S_2 + H_2S = As_2S_5 + 4H_2O, \text{ etc.}$$

When, therefore, in these circumstances, the arsenic is all down, the precipitate will consist of a mechanical mixture of arsenic pentasulphide, arsenic trisulphide and sulphur, and this is in accordance with the facts.

The changes which occur when sulphuretted hydrogen acts on arsenic acid remind us forcibly of the reactions of organic chemistry. Are the former analogous to esterifications,[1] or are they

[1] $R.OH + CH_3.C(=O)-OH = CH_3.C(OR)(-O-H)(-OH) \rightarrowtail CH_3.C(=O)-OR + HOH.$

true ionic reactions? I firmly believe that they are ionic reactions, not simple but complex ionic reactions. However, to settle the matter beyond a doubt we need more facts. If the changes are additions and splittings, the mechanism of the various steps can be represented by the following equations:



Let us now endeavor to see if the electrolytic dissociation theory can be applied to an interpretation of the reactions.

The various hydrogen atoms of a polybasic acid have different values as regards the strength of the latter. The first atom of hydrogen in a molecule of such an acid is always that of a stronger acid than the second, while the third and fourth follow in the same order. The first step in the dissociation of a polybasic acid is the most important one, and the amount of this dissociation depends upon the relative strength of the acid. Now since arsenic acid is a weak acid,[1] the dissociation which it undergoes when we dissolve

[1] According to Walden's measurements, it is about 20 per cent. dissociated in 01. molar sol.

it in water will be necessarily small, so that the second and third steps in the breaking-down of the molecule can be neglected:

$$H_3AsO_4 \rightleftarrows H_2AsO'_4 + H^{\cdot}$$

But since arsenic exhibits basic as well as acid properties, it seems reasonable to assume that arsenic acid can also undergo a slight basic dissociation. What has just been said in regard to the dissociation of a polybasic acid is correspondingly true of a polyacid base. The first step in the dissociation is the important one and since arsenic acid, if looked upon as a base, is undoubtedly a very weak one, the second and third stages in the cleavage of the molecule can be disregarded. The basic dissociation of the compound would be represented thus:

$$H_3AsO_4 \rightleftarrows H_2AsO^{\cdot}_3 + OH'.$$

We may indicate both dissociations in this way:

$$OH' + H_2AsO^{\cdot}_3 \rightleftarrows H_3AsO_4 \rightleftarrows H_2AsO_4' + H^{\cdot}.$$

The foregoing equation represents then, the equilibrium existing in an aqueous solution of arsenic acid. The $C_{(OH')}$ is extremely small, less even than the $C_{(OH')}$ in water, because, in general,

$$C_{(H^{\cdot})} \times C_{(OH')} = K$$

and if we increase the $C_{(H^{\cdot})}$ the $C_{(OH')}$ will correspondingly decrease. An aqueous solution of arsenic acid has a far greater value of $C_{(H^{\cdot})}$ than pure water, and hence a much less value of $C_{(OH')}$.

Again, consider the expression

$$C_{(OH')} \times C_{(H_2AsO_3^{\cdot})} = K_1 \times C_{(H_3AsO_4)}.$$

Here the numerical value of K_1 is, of course, unknown, but even though it is undoubtedly very small, the value of $C_{(H_2AsO_3^{\cdot})}$ may still be appreciable, since the value of $C_{(OH')}$ is kept so extremely low by the considerable concentration of the $H^{\cdot}$ ions.

Allow the solution to be saturated and *kept* saturated with sulphuretted hydrogen,

$$H_2S \rightleftarrows H^{\cdot} + SH'.$$

The degree of dissociation is slight, for sulphuretted hydrogen is a very weak acid. The dissociation, too, will be depressed to some extent by the hydrogen ions of the arsenic acid, seeing that arsenic acid is a stronger acid than sulphuretted hydrogen. It is

plain, however, that the $C_{(OH')}$ in the solution will be far less than the $C_{(SH')}$.

If, now, some SH′ ions and some $H_2AsO'_3$ ions unite, some undissociated monosulphoxyarsenic acid will be formed, the equilibrium of the system will be disturbed, more $H_2AsO'_3$ ions will appear and more monosulphoxyarsenic acid will come into existence. In spite, therefore, of the very small value of $C_{(H_2AsO'_3)}$ at the moment when the sulphuretted hydrogen is introduced into the solution, the resulting $C_{(SH')}$ value will soon become sufficiently great to occasion the production of a measurable amount of monosulphoxyarsenic acid,

$$H_2AsO'_3 + SH' = H_3AsO_3S.$$

Monosulphoxyarsenic acid is capable of undergoing two kinds of basic dissociation:

$$1.\ H_3AsO_3S \rightleftharpoons SH' + H_2AsO'_3$$

and

$$2.\ H_3AsO_3S \rightleftharpoons OH' + H_2AsO_3S'.$$

Since the SH′ ions are far in excess of the OH′ ions, the second kind of dissociation would probably predominate and since the solution is kept saturated with sulphuretted hydrogen, some H_2AsO_2S' ions will combine with SH′ ions and some undissociated disulphoxyarsenic acid will be produced. The disulphoxyarsenic acid will, in its turn, yield $H_2AsOS'_2$ and OH′ ions, and $H_2AsOS'_2$ and SH′ will unite to form some trisulphoxyarsenic acid, and so on to the end.

The small ionic concentrations and the appearance and disappearance of the complex ions are quite in harmony with the sluggishness of the reactions, and a consideration of the rates of the various transformations would indicate the existence, at some time during the interactions, of a considerable concentration of monosulphoxyarsenic acid; later the maximum concentration of the disulphoxyarsenic acid, which, however, would be less than the maximum concentration of the former, and later still the maximum concentration of the trisulphoxy-compound, which indications are in accordance with the facts.

Now Brauner and Tomicek,[1] as well as Neher,[2] have shown that strong acids (HCl and H_2SO_4) accelerate, in a most pronounced way, the transformation of arsenic acid by means of sulphuretted hydrogen into sulpharsenic acid, so the question at once arises,

[1] *J. Chem. Soc.*, **53**, 145.
[2] *Ztschr. anal. Chem.*, **32**, 45.

What role do these strong acids play? In the light of what I have already said it is evident that the increase in the value of $C_{(H')}$, due to the presence of such acids, serves to decrease the value of $C_{(OH')}$ and so promotes the basic dissociation of the arsenic acid. These strong acids will, of course, lower the dissociation of the sulphuretted hydrogen, but we must remember that while the value of $C_{(SH')}$ undoubtedly falls off, that of $C_{(OH')}$ is reduced in a vastly greater proportion.

Given then an aqueous solution of arsenic acid, saturated and kept saturated with sulphuretted hydrogen, or given an aqueous solution of arsenic acid containing a considerable amount of a strong mineral acid (HCl) and saturated and kept saturated with sulphuretted hydrogen, and omitting any consideration of the second and third steps in the basic dissociation, we may represent the successive reactions in the following way:

1. $H_3AsO_4 \rightleftarrows H_2AsO'_4 + OH'$
2. $H_2AsO'_4 + SH' = H_3AsO_3S$[1]
3. $H_3AsO_3S \rightleftarrows H_2AsO_2S' + OH'$
4. $H_2AsO_2S + SH' = H_3AsO_2S_2$
5. $H_3AsO_2S_2 \rightleftarrows H_2AsOS'_2 + OH'$
6. $H_2AsOS'_2 + SH' = H_3AsOS_3$
7. $H_3AsOS_3 \rightleftarrows H_2AsS'_3 + OH'$
8. $H_2AsS'_3 + SH' = H_3AsS_4$

The sulpharsenic acid then breaks down:

$$2H_3AsS_4 = As_2S_5 + 3H_2S.$$

Neher[1] observed a number of years ago, and his results have been confirmed by Weinland[2] and myself,[3] that when arsenic acid is present in a mixture of two volumes of strongest aqueous hydrochloric acid and one volume of water, sulphuretted hydrogen precipitates the arsenic almost instantly as the pentasulphide. If

[1] Since the structural formula for monosulphoxyarsenic acid is undoubtedly $S = As(OH)_3$, it would, perhaps, be more rational to assume, in the solution, the presence of the normal compound $As(OH)_5$.

$$As(OH)_5 \rightleftarrows As(OH)'_4 + OH'$$

$$As(OH)'_4 + SH' = As\begin{matrix}OH\\OH\\OH\\O\,H\\S\,H\end{matrix} \rightarrow S = As\begin{matrix}OH\\OH\\OH\end{matrix} + HOH, \text{ etc.}$$

[2] *Ztschr. anal. Chem.*, **32**, 45.

[3] *Ztschr. anorg. Chem.*, **14**, 44.

the rapid formation of the pentasulphide is in this case due to the $C_{(H^+)}$ then any strong acid which would give as great a $C_{(H^+)}$ as hydrochloric acid should have a similar effect, providing, of course, the anions occasion no disturbing by-reactions. Neher tried sulphuric acid and found that it acted in a manner analogous to hydrochloric acid. Nitric acid must be excluded but the behavior of other strong acids would prove interesting. There is, however, another way of looking at the matter. Assuming, as we have done, that arsenic acid can act as a very weak base, in the presence of a great excess of such a strong acid as hydrochloric acid, the production of the salt arsenic pentachloride[1] is at least not impossible. It would doubtlessly be formed by stages but the final product of the reaction we may assume to be the pentachloride:

$$AsCl_5 \rightleftarrows As^{\cdots\cdots} + 5Cl$$

$$2As^{\cdots\cdots} + 10SH' = 2H_3AsS_4 + 2H_2S \rightarrowtail As_2S_5 + 5H_2S.$$

If the train of reasoning above given be correct, the facts cited in my paper in the *Zeitschrift für anorganische Chemie* find a very satisfactory explanation in terms of the electrolytic dissociation theory.

In closing I wish to express my sincere thanks to Dr. George A. Hulett, of the University of Michigan, for his kindness in suggesting to me the possibility of arsenic acid undergoing a slight basic dissociation, as well as for the friendly interest he has shown in my work.

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THE SOLUBILITY OF GYPSUM.

BY GEORGE A. HULETT AND LUCIUS E. ALLEN.

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ALTHOUGH the solubility of the substance $CaSO_4.2H_2O$ has been the subject of investigation by many careful workers, the results vary widely, while the experimental errors are comparatively small. The cause of these discrepancies was pointed out by Hulett,[2] in the course of an investigation of the influence of

[1] In this case we would have to assume that the aqueous solution of arsenic acid contains the normal compound H_5AsO_5.

[2] *Zischr. phys. Chem.*, **37**, 385.

surface-tension on solubility, where it was shown that the energy existing on the surface between a solid and its saturated solution is a measurable factor of the solubility. The concentration of the solution in equilibrium with a curved surface is different from that in equilibrium with a plane surface. Attention was called to a *normally saturated solution; i. e.*, the solution which is in equilibrium with a plane surface of the solid, and it was shown that a convex surface will show greater solubility and a concave one a less solubility than a plane surface; *e. g.*, if the solid is finely divided the solubility will be noticeably greater; in the case of gypsum[1] the solubility was increased 20 per cent. by decreasing the size of the particles to 0.3 micron. When larger pieces of gypsum were placed in a flask with water and rotated in a thermostat—the usual method of saturating a solution—the concentration became 5 per cent. greater than a normally saturated solution at the same temperature, because gypsum is a very soft mineral and is easily ground to powder. It was therefore found necessary to remove all the small particles and then cause the liquid to rotate over the solid, but without disturbing it.

At 25° a normally saturated solution of gypsum contained 15.33 milligram-molecules in a liter (a supersaturated solution was stirred in contact with the gypsum plates at 25° C. and decreased in concentration to 15.33 milligram-molecules to a liter, leaving no doubt as to the question of equilibrium having been established). All previous determinations of the solubility of gypsum vary more or less from the above figure for 25° C., and the results are greater than 15.33 milligram-molecules in a liter, indicating that where care had been taken to avoid supersaturation, the solutions analyzed were still those in equilibrium with more or less convex surfaces, due to the fact that too finely divided gypsum had been used. In view of the above facts and the special importance of the solubility curve of gypsum, a careful determination of the concentrations of normally saturated solutions of gypsum was undertaken.

SOLUBILITY IN GENERAL.

The question as to how solubility should be expressed has received very little attention and with the numerous methods in vogue there is little uniformity in the published results. The densities of

[1] *Ztschr. phys. Chem.*, **37**, 388.

the solutions worked with are seldom given and the lack of these data often excludes comparisons or recalculations. In the case of a slightly soluble substance like gypsum (2.4 grams per liter) the results are mostly given as parts of water to dissolve 1 part of gypsum, while from the context it appears that the calcium sulphate was determined from a volume of the solution. The question of the density of the solutions is not mentioned so the results are in reality volumes of solution which contain 1 gram of calcium sulphate, or gypsum, as the case may be. The error is not negligible and increases with the temperature.

If a quantity of the solution is weighed out in a weighing bottle[1] and the solute (the dissolved substance) is determined gravimetrically, the results are very definite as far as the masses of the solvent and the solute are concerned and the results are to be expressed as parts of solute to 100 parts of solution, or parts of solvent for 1 part of solute, or better still as gram-molecules dissolved by 100 gram-molecules of solvent, but the density is still needed as a control and to allow of comparison with results determined from volume. The results expressed as parts of solute to 100 parts of solution yield for the temperature curve nearly straight lines,[2] but not in all cases, and while there may be some advantage in locating a break or the appearance of a new phase when the curves are straight lines, still there is so little known at present concerning the relation of solubility to other magnitudes that this choice would be quite arbitrary.

A pipette is an exceedingly accurate instrument if graduated *to volume* (not grams water weighed in air), and the contents rinsed out. The volume taken is thus diluted by the rinsing water but the mass of the solute is determined gravimetrically. If the pipette is provided with a ground glass cap for the lower end, it serves at the same time as a pycnometer, or a good-sized pycnometer may be used for a pipette, first determining the density then washing out the solution and determining the solute analytically. In this manner not only the weight of the solution and solute are obtained but also the volume of the solution and the results can be expressed as gram-molecules of the solute in a liter, or in any manner desired. Since from the modern standpoint the dissolved substance is regarded as a gas,

[1] Van't Hoff: Vorlesungen, p 24.
[2] Etard: *Compt. rend.*, **108**, 176.

there is much to be said in favor of expressing the solubility results as concentration or gram-molecules in a liter of the solution. A knowledge of the vapor-pressure of the solution is also very desirable as it allows of a calculation of the osmotic pressure and the application of other thermodynamic relations. With electrolytes conductivity is also expressed in terms of concentration, while solutions for volumetric analysis, with which all chemists are familiar, consider only the volume and mass of the solute. Complete data would include a determination of the mass, volume, and concentration of the normally saturated solution; the conductivity, if electrolyte, should be taken as a control and also, if possible, the vapor-tension.

THERMOSTATS.

For temperatures below that of the surroundings, there seems to be no satisfactory device for accurately controlling the temperature. In using the ordinary Ostwald regulator and a cooling tube in the bath, a good deal of tap water is required. This is due to the effect of the small flame, which continually burns beneath the bath. If we do away with this flame and have the bath well covered with felt and the top protected by glass and felt, then a very little ice-water from a convenient tank will keep the temperature down. A short coil of very fine platinum wire is arranged above the mouth of the regulator burner and by means of the second hand of a clock, which makes and breaks an electric current, this platinum wire is made to glow an instant every minute; now the regulator can shut the gas off entirely and when let on again the platinum which glows once every minute will light it. With our large 45-liter bath well protected with felt, the temperature can be maintained quite as accurately below as above room temperature and with very little ice-water dropping into the bath.

The thermostat used at zero consisted of a large tank of 45 liters' capacity, filled with fine cracked ice. The Bunsen flask used for solution was sunk into the ice and stood on a tripod. The bath was covered on all sides with a thick layer of felt and the ice kept for fully twenty-four hours without replenishing, the temperature remaining almost absolutely constant.

For all temperatures above room temperature, except at 100° C., a large bath was used which was covered on the sides with

several thicknesses of asbestos, the bottom being also covered, with the exception of a small circular place in the center for the flame, and the top was covered with glass plates and asbestos. The thermostat was let into a table so that it projected about 10 cm. above the top. Below, and extending from the table to the floor, four large sheets of asbestos enclosed the lower part of the bath, thus preventing draughts, etc., from effecting the temperature. This bath enabled us to keep within 0.1° even at 75°.

Jena flasks, Erlenmeyer form, were used, the flask being immersed to the neck in the bath and covered so that there was no distillation and condensation in the neck. The temperature was controlled to within 0.1 or 0.05 of a degree during saturation. A Shultz stirrer was used in the flask and the height of the stirrer was so regulated that the arms did not disturb the gypsum plates, but kept the solution in a slow but steady motion over them, the stirrer running about 50 revolutions per minute.

The bath used for 100° C. was much smaller than those used for the other temperatures, being of about 7 liters' capacity. The bath was filled about a third full of water so that the flask was not immersed in the boiling water, but was completely surrounded with steam. A long-necked Florence flask (Jena) was used and to prevent evaporation, a test-tube which fitted nicely into the neck of the flask, was provided with a short tube below for the passage of the stirrer-rod; the stirrer-rod was supported also by the cork in the upper part of the test-tube. The flask was thus closed off at the point where the neck joined the flask and was so full of water that there was little free surface for evaporation; this scheme effectually prevented distillation from the solution even at 100°.

All density determinations were made with a Sprengel-Ostwald pycnometer, capacity 25 cm^3. The end of the capillary arm of this pycnometer was provided with a ground-on cap to prevent loss by evaporation or in handling. As a control, the density of water was determined at the temperature of the experiment, and then the gypsum solution, under exactly the same conditions. The results were calculated to weight in vacuum and from the known density of water, the density of the solution was calculated to $\frac{mass}{cm^3}$, that is, referred to water at 4° C. Duplicates agreed to the fifth decimal place, leaving the sixth uncertain.

ANALYTICAL METHODS.

The analytical results were based on the amount of anhydrous calcium sulphate in 100 cm^3 (volume) of the gypsum solution saturated at a given temperature. The samples for analysis were taken from the solution flask while still immersed in the constant water-bath, by filling an accurately standardized 100 cm^3 (volume) pipette and at once allowing the solution to run into a weighed platinum dish, thoroughly rinsing the pipette with distilled water. The duplicate samples were then evaporated to dryness on water-baths, using condensing funnels to exclude dust. When evaporated to dryness the platinum dishes were placed in a specially constructed glowing oven, made as follows: A cylindrical sheet-iron or tin jacket was covered with asbestos, the seams of the asbestos being cemented together with a little sodium silicate. A conical cover was made, covered in the same manner, and having a small hole in the apex to allow of the escape of the gases of combustion. Within the jacket and about in the center was supported a casserole in which the platinum dish was placed, standing on three small pieces of porcelain. The casserole was then covered with an inverted evaporating dish. The whole apparatus was supported on a ring stand and heated from underneath with a Detroit burner. In this way the samples of gypsum could be carefully heated and the temperature within the casserole was sufficient to completely dehydrate the gypsum, but too low to decompose the calcium sulphate as the following experiment showed.

A known weight, 0.8788 gram, of the gypsum plates were placed in a weighed platinum dish and put in the glowing oven. After glowing for one and three-quarter hours, the platinum dish was cooled and weighed, giving the following weight—51.5600 grams; the dish was replaced in the oven and glowed for two hours under the same conditions and again cooled and weighed, giving the same weight as before—51.5600 grams. The loss of water was within 0.1 per cent. of the theoretical. It was noticed that the weight of the calcium sulphate would increase if left for a little time in the air; hence, it seems to be slightly hygroscopic and the weighings were made *rapidly*. The first heating gave the approximate weight and, having this, the second and following heatings could be done so rapidly that the error was entirely negligible. The residue of the above experiment was digested with a

little water but showed no suggestion of an alkaline reaction, while the weight indicated that it had not lost sulphur trioxide, nor did it lose weight on continued heating.

The gypsum used in this work was the same as that used in the previous work on gypsum.[1] It was from a very large and perfectly clear crystal from Wyoming. Analysis of a saturated solution of this gypsum showed no trace of chlorine. The gypsum was broken up into thin plates of 1.0 to 0.5 mm. thickness, and all fine particles were removed by repeated washing and decantation with distilled water. The water used was obtained by redistilling distilled water after addition of barium hydroxide,[2] only water having a conductivity of less than 1.5×10^{-6} being used for the solution of the gypsum. The capacity of the cells used in this work was determined by a N/50 potassium chloride solution, using the above water and carefully purified and fused potassium chloride. The results represent the conductivity of a cubic centimeter of the solution compared to a solution, 1 cc. of which has a resistance at the temperature of 1 ohm ($106.3 \frac{cm.}{mm.^2}$ Hg at 0°) (Kohlrausch unit).

The following table (I) gives the results obtained in this investigation; column II gives the actual weights, in duplicate, of the calcium sulphate (heated to constant weight as above described) from 100 cm^3 of the solution measured at the temperature of the experiment. Column III gives the calculated milligram-molecules in a liter at the temperature of the experiment. The result for 107°, 11.39 milligram-molecules in a liter, is exterpolated, and the course of the curve I (Fig. I) is so uniform that this figure is probably correct to the first decimal place. This point is the end of the gypsum curve since van't Hoff and Armstrong[3] have shown that at this temperature the vapor-pressure of gypsum equals that of water and (since the vapor-pressure of the gypsum solution varies so slightly from that of water) this is the temperature at which gypsum turns to halfhydrate. At 107°, under normal conditions, there is a break in the curve, and the continuation is the curve which is in equilibrium with $CaSO_4.\frac{1}{2}H_2O$.

Column IV gives the density $\frac{mass}{cm^3}$ at the temperature of the experiment; these data allow of a recalculation of the concentra-

[1] *Loc. cit.*
[2] Hulett: *Ztschr. phys. Chem.*, **33**, 297.
[3] *Sitz. Ber.*, (1900), p. 559.

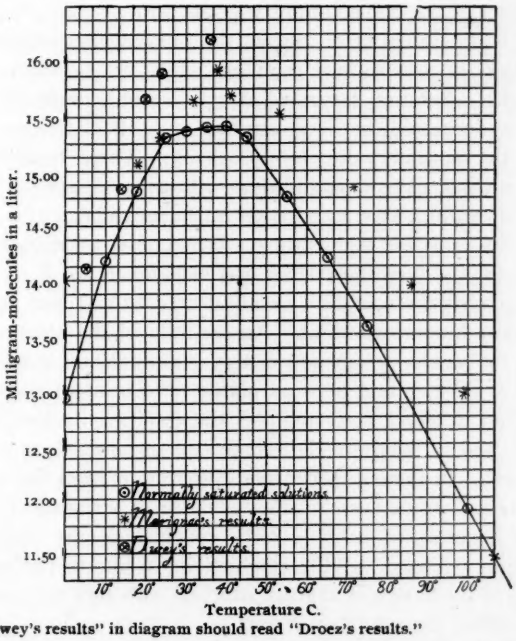
TABLE I.

I. Temperature.	II. Grams $CaSO_4$ in 100 cm^3 solution. Duplicate.	III. Millimolecules for 1 liter.	IV. Density of solution. Mass / cm^3. For T° C.	V. λ for T° C.	VI. λ for 25° C.	VII. Time for conductivity to become constant. Minutes.
0°	{ 0.1760 / 0.1758 }	12.926	1.001970	0.000945	0.001958	..
10°	{ 0.1931 / 0.1926 }	14.177	1.001727	0.001486	0.002080	90
18°	{ 0.2017 / 0.2015 }	14.817	1.000590	0.001830	...	80
25°	{ 0.2083 / 0.2078 }	15.295	0.999109	0.002206	0.002206	75
30°	{ 0.2092 / 0.2089 }	15.361	0.997891	0.002445	...	60
35°	{ 0.2096 / 0.2096 }	15.405	0.996122	0.00268	0.002226	50
40°	{ 0.2097 / 0.2097 }	15.413	0.99439	0.002845	0.002232	45
45°	{ 0.2086 / 0.2081 }	15.310	0.992370	0.003045	0.002264	60
55°	{ 0.2012 / 0.2007 }	14.765	0.98796	0.003375	...	40
65.3	{ 0.1934 / 0.1930 }	14.200	0.98256	0.003603	...	45
75°	{ 0.1851 / 0.1844 }	13.575	0.977724	...	...	40
100°	{ 0.1624 / 0.1615 }	11.900	...	...	...	..
107°	...	(11.390)	...	...	...	..

tion to any other standard. The weights are all corrected to vacuum. The densities differ rather uniformly from water by + 0.002. At 25° C. for example, from the density and the mass of solute (regarding it as calcium sulphate and specific gravity 3), we find the density of the solvent slightly greater than water (0.99773) instead of (0.99710), that is, the condensation of the solvent is very slight, only 0.00063.

Columns V and VI give the electrical conductivity in the standard unit. These were taken primarily to determine when the solution was saturated. Into a 1½ liter Erlenmeyer flask with the bottom covered 1 cm. deep with small gypsum plates was brought about 1 liter of conductivity water, all at the temperature of the bath, and the liquid rotated about fifty times per minute, and since the gypsum plates were not disturbed the solution above was always

clear. From this every five or ten minutes (at first), 10 cm³ was removed and its conductivity determined. Under these conditions, which could not be regarded as overfavorable for rapid saturation, it was found that saturation took place in from forty to ninety minutes, depending on the temperature, as can be seen in column VII. Of course the rate of solution depends on several factors, but in the case of gypsum it seems to be fairly rapid, and this agrees with the observations of Bruner and Tallocyko.[1]



"Dwey's results" in diagram should read "Droez's results."

Cameron[2] assumes that the rate of solution is very slow and endeavors to explain the discrepancies in the published solubility results as due to undersaturated solutions, whereas the results generally are on the other side of normally saturated solutions.

The preceding table gives the results of normally saturated solutions starting from water and gypsum and assuming that equilibrium was reached when the conductivity of the liquid was

[1] *Zischr. anorg. Chem.*, **28**, 320.
[2] *J. Phys. Chem.*, **5**, 567.

constant, although in all cases the liquid was rotated over the gypsum plates for an extra hour or two before the analysis was made. A solution saturated at 25° C. (or which from conductivity showed 15.29 milligram-molecules per liter) was brought to 0° and rotated in contact with the gypsum plates. The conductivity slowly decreased but it required two days, or forty-eight hours to become constant, and analysis gave for 100 cm^3 0.1758 gram calcium sulphate, whereas the solution starting from water and gypsum at 0° C. gave 0.1760 and 0.1758 gram while the conductivity of the two solutions was the same.

At 25° C. the system water-gypsum showed a constant conductivity of 0.002206 in seventy-five minutes, while the previous work[1] showed that a solution saturated at 35° C. and brought to 25° C. gradually decreased in conductivity, and after twelve hours reached the normal value $\lambda = 0.002208$. These results show that our method gave us equilibrium, but it was deemed advisable to test this point above the change in the solubility curve at 40° C., so 50° C. was the temperature selected; first a saturation was made at 38° C.; then the system was brought to 50° C., where it was found that the solubility slowly decreased and next morning had already become constant. An analysis of the solution gave per 100 cm^3 0.2049 gram and 0.2045 gram calcium sulphate respectively. Water and gypsum plates were brought together at 50° C., and in about forty minutes the conductivity had become constant, and an analysis showed 0.2040 gram calcium sulphate in 100 cm^3. In these experiments evaporation from the solution was prevented in the same manner as in the experiment at 100° C.

These experiments seem to settle conclusively the question of equilibrium. Above 50° the conductivity seems to indicate that the glass of the flask was slightly attacked, although not enough to sensibly affect the solubility results.

The early works on the solubility of gypsum have only a historical interest, although the result given by Giese[2] of 380 parts of cold water to dissolve 1 gram of gypsum is not far wrong for room temperature; but 388 parts of boiling water to 1 of gypsum is quite wrong. Tipp[3] also gives 388 parts of water to 1 of gypsum at 15°-20° C.

[1] *Ztschr. phys. Chem.*, **37**, 391.
[2] Auflage Gmelin's Handbuch, Vol. V., 183.
[3] *Jahresbericht*, (1864), **5**, 325.

Marignac[1] showed that it was exceedingly easy to obtain a supersaturated solution of gypsum and that such a solution was very slow to come to equilibrium, even in the presence of an excess of the solid gypsum. Marignac made determinations between 0° and 100°, taking care to have an excess of finely divided gypsum uniformly distributed through the solution, and the system was undoubtedly in equilibrium before a part of the clear solution was analyzed. He was able to show that the results of his predecessors were affected by the phenomena of supersaturation.

Droez[2] confirmed Marignac's results and added several of his own. He especially showed that the equilibrium could be reached from either side, emphasizing the necessity of an excess of the finely divided gypsum and constant agitation. Droez also took account of the density of water in his calculations. He assumed the density of his solution to be the same as that of water at the same temperature, and gave a table of solubilities from 0° to 100° C. from a curve of his and Marignac's results. Both of these workers avoided supersaturation in the sense that their solutions were in equilibrium with the solid present. Still, from the method of these experiments and the results, the solid must have

TABLE II.

	I.	II.	III.	IV.
T°.	Poggiale.	Marignac.	Droez.	Normally saturated solutions.
0	15.06	14.00	...	12.91
5.5	...	...	14.11	13.56
14.2	...	...	14.83	14.50
18	...	15.06	...	14.81
19.5	...	...	15.66	14.88
20	17.72	...	...	14.95
24	...	15.30	15.87	15.23
32	...	15.64	...	15.38
35	18.75	...	...	15.40
36	...	...	16.19	15.41
38	...	15.79	..	115.41
41	...	15.71	...	15.39
53	...	15.52	...	14.85
72	...	14.86	...	12.70
86	...	13.94	...	12.70
99	...	12.89	...	11.95
100	...	...	...	11.90

[1] *Ann. chim. phys.*, (5) **1**, 274 (1874).
[2] *Ber. d. chem. Ges.*, (1877), p. 330.

been very finely divided, that is, having some particles less than 2 microns in diameter since their solutions were about 5 per cent. more concentrated than normally saturated solutions. The results of these two workers have been accepted as the most reliable, so they have been calculated to millimolecules per liter and given in Table II (preceding page), together with the concentrations of normally saturated solutions taken from the curve of our results.

Kohlrausch and Rose[1] give results of conductivity of solutions saturated at various temperatures. A comparison of these data with the conductivity of known solutions[2] shows that their solutions were some 4 per cent. too concentrated. There are a great many determinations of the solubility of gypsum or crystallized $CaSO_4.2H_2O$ by various workers, and even where care was taken to avoid supersaturation, the results generally distinctly show the influence of surface-tension. There are two exceptions, Cossa and Church, who made determinations at about 20° and 13°; their results are 10.5 per cent. and 12 per cent. respectively *below* the normally saturated solutions. We have not been able to consult the original publications so we cannot judge of the material or the method used. The previous work[3] showed that in the case of gypsum the surface-tension plays a decided rôle in the solubility, for it was found possible to increase the solubility (at 25°) 20 per cent. by grinding the gypsum powder in an agate mortar, but the system so obtained was not in final equilibrium, since the smaller particles grew smaller and disappeared while the larger ones grew in size. This is, however, a slow process[4] with gypsum and does not reach final equilibrium (the normally saturated solution) in five days, while if the stirring is too rapid, the abrasion from the soft gypsum continually yields a fine powder, and a normally saturated solution is never attained. Plates of gypsum rotated with water in a flask, as is ordinarily done in solubility determinations, will easily yield a 5 per cent. too great solubility. On the other hand the results here obtained show that slowly rotating a liquid over the plates will give a saturated solution in about an hour's time. These facts give a satisfactory explanation of the irregularities in the published determinations.

[1] *Ztschr. phys. Chem.*, **12**.
[2] *Ibid.*, **37**, 371.
[3] *Ibid.*, **37**, 392.
[4] *Loc. cit.*, p. 394.

The solubility curve of gypsum is of special interest on account of the change in the direction of the curve. This fact was discovered by the early workers, and from Marignac's and Droez's results the maximum solubility is given at 38° C. while the curve of the results here obtained indicates 40° C. as the temperature at which there is the greatest concentration. From here the concentration decreases with the temperature and at 90° is the same as at 0°, while at 107° it has decreased some 12 per cent. further. There seems to be no break in the curve at 40° as we had expected to find, while the vapor-pressure curve of water compared to that of gypsum, plotted from the interesting results of van't Hoff and Armstrong,[1] show a perfectly uniformly increasing difference from 0° to 85°, where the vapor-pressure of water is some 85 mm. greater than that of gypsum. At 40° the difference is 29 mm. From 85° on the difference decreases, and at 107° the lines cross and the half hydrate appears (a saturated solution of gypsum must have a vapor-pressure that is only a few hundredths of a millimeter less than that of pure water). The uniformity of the vapor-pressure curve of gypsum excludes the idea of explaining the change at 40° (from increasing to decreasing solubility) by assuming the appearance of a new phase. Thermodynamics connects this change at 40° with the change of the sign of the heat of solution. This question has been thoroughly discussed by van't Hoff[2] where the case of gypsum is considered. It is to be noted that this is a thermodynamic relation and while it is experimentally supported by the observations of Berthelot on the heat of precipitation of $CaSO_4.2H_2O$ above and below 40°, we are still in the dark as to why the curve takes a downward curve at 40°.

In the case of slightly soluble substances the effect of the dissolved substance on the solvent can be neglected, while in the case of more soluble substances the nearly saturated solution is a quite different agent from the pure solvent,[3] so it seems probable that general relations will first be found in connection with less soluble substances and the results of this paper indicate that there is need of a careful redetermination of such data with due regard to the influence of surface-tension.

DEPARTMENT OF GENERAL CHEMISTRY,
UNIVERSITY OF MICHIGAN,
March, 1902.

[1] *Sitz. Ber.* (1900), p. 559.
[2] Vorlesungen, p. 31.
[3] Nernst: "Theoretische Chemie," p. 445.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(FOURTH PAPER.)

BY HENRY L. WHEELER AND TREAT B. JOHNSON.

Received April 11, 1902.

THE work described in this paper was undertaken with the object of investigating the behavior of some tertiary halides towards alcoholic solutions of potassium thiocyanate. Up to the present time no tertiary alkyl halide has been found to give an isothiocyanate or mustard oil. This property has only been observed in the case of the primary allyl halides and the secondary diphenylmethyl bromide. In fact this subject has hitherto received little attention. Of the three tertiary halides that have been examined triphenylmethyl bromide and α-bromisobutyric ethyl ester gave normal thiocyanates while tricarbethoxymethane failed to react.[1]

The tertiary halides which we now discuss comprise all the possible compounds formed by substituting the positive group methyl, and the negative radicals, phenyl and carbethoxyl, $-CO.OC_2H_5$, for hydrogen in methyl bromide.[2] There are ten combinations to be considered; and among these, it will be noticed, are the above three tertiary forms that have already been examined:

I. $BrC(CH_3)_3$	VI. $BrCCH_3(CO_2C_2H_5)_2$
II. $BrC(CH_3)_2C_6H_5$	VII. $BrC.CH_3.C_6H_5.CO_2CH_3$
III. $BrCCH_3(C_6H_5)_2$	VIII. $BrC(CO_2C_2H_5)_3$
IV. $BrC(C_6H_5)_3$	IX. $BrCC_6H_5(CO_2C_2H_5)_2$
V. $BrC(CH_3)_2CO_2C_2H_5$	X. $ClC(C_6H_5)_2CO_2C_2H_5$

The investigation has shown that six of these compounds give normal thiocyanates, while the remaining four give neither normal or isothiocyanates.

Tertiary butyl bromide (I) reacted smoothly with alcoholic

[1] Since the above was written Crocker has found that picryl chloride gives an isothiocyanate. *Jour. Chem. Soc.* (London), **81**, 436 (1902).

[2] In one case (VII) the methyl ester was used and in another (X) the chloride instead of the bromide was employed; experience has shown that the bromides react more readily than the chlorides.

potassium thiocyanate, and the product was shown to be a normal thiocyanate by combining it with thioacetic acid, whereupon acetyl dithioisobutyl urethane, $CH_3CONHCSSC_4H_9$, was obtained.

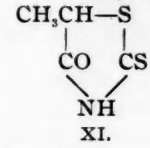
1′-Bromisopropyl benzene (II), 1′-brom-1,1-diphenylethane, (III), 1′-bromhydratropicmethyl ester (VII), and tricarbethoxymethyl bromide (VIII) reacted readily with, or were decomposed by, potassium thiocyanate, and a bright yellow, amorphous precipitate separated which had the properties of the so-called pseudocyanogen sulphide. These bromides therefore act like free bromine on potassium thiocyanate. The behavior of tricarbethoxymethyl bromide, in reacting immediately in the cold, is in strong contrast to that of the chloride, which showed little tendency to react even on heating for a number of hours.

Triphenylmethyl bromide (IV), as previously stated, gave a normal thiocyanate. In this case the rhodanide formed thiol esters with thioacetic and thiobenzoic acids.

α-Bromisobutyric ethyl ester (V) also gave a normal thiocyanate. This was shown by boiling the product with hydrochloric acid, whereupon α-μ-diketo-β-dimethyltetrahydrothiazole, was obtained.

Methylbrommalonic ester (VI) readily reacted with potassium thiocyanate, while ethyl chlormalonic ester remained unaltered even when heated with potassium thiocyanate to 140°-145° for a number of hours. When the product, in the case of methylbrommalonic ester was warmed with thioacetic acid, a thick oil was obtained which, on dissolving in alkali and precipitating with hydrochloric acid, gave α-keto-μ sulpho-β-methylthiazolidine, the so-called α-rhodaninpropionic acid.[2] The structure of this is represented by formula XI. That the rhodanide is a normal thiocyanate is shown by the fact that the reaction took place as follows:

$$CH_3CONHCSSCCH_3(CO_2C_2H_5)_2 + NaOH + H_2O =$$
$$C_4H_5ONS_2 + CH_3COONa + CO_2 + 2C_2H_5OH.$$



XI.

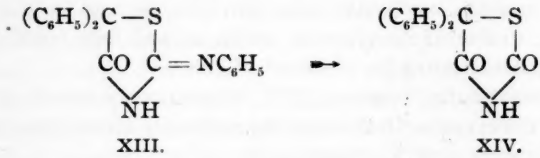
XII.

[1] *Am. Chem. J.*, **24**, 78 (1900).

[2] Berlinerblau: *Ber. d. chem. Ges.*, **19**, 125.

Bromphenylmalonic ester (IX) reacted smoothly with potassium thiocyanate, and the product with thioacetic acid and alkali behaved in a similar manner, inasmuch as α-keto-μ-sulpho-β-phenylthiazolidine (XII) was obtained.

Diphenylchlorethyl acetate (X) gave the first and only rhodanide that has failed to react with thio acids. It reacted, however, with aniline, yielding triphenylpseudothiohydantoïn (XIII). On warming the latter with alcoholic hydrochloric acid, α-μ-diketo-β-diphenyl tetrahydrothiazole was obtained (XIV).

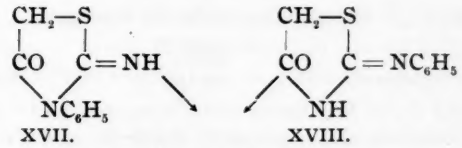


XIII. XIV.

The behavior of this hydantoïn with hydrochloric acid differs from that of the pseudothiohydantoïn from phenylthiocyanethyl acetate,[1] inasmuch as the latter, under certain conditions, gives up ammonia and not aniline on boiling with hydrochloric acid; generally, however, a mixture is obtained. The behavior of phenylpseudothiohydantoïn with hydrochloric acid has been supposed to show that the compound has the structure represented by formula XVII.

We have found that this long-known phenylpseudothiohydantoïn which, according to Meyer,[2] Liebermann,[3] and Dixon,[4] gives α,μ-diketo-N-phenyltetrahydrothioazole ("phenylsenfoelglycolid"), formula XXI, with hydrochloric acid, also gives α,μ-diketotetrahydrothiazole (XX). It follows from this that the reaction with hydrochloric acid can not be used to decide the structure of these thiohydantoïns. Both of the theoretically possible isomeric phenylpseudothiohydantoïns, (XVII) and (XVIII), for example, can give phenylthiohydantoic acid (XIX), and this can be decomposed into the two tetrahydrothiazoles that are actually obtained:

[1] *Am. Chem. J.*, **26**, 353 (1901).
[2] *Ber. d. chem. Ges.*, **14**, 1661 (1881).
[3] *Ann. Chem.* (Liebig), **207**, 129 (1881).
[4] *J. Chem. Soc.* (London), **71**, 620 (1897).



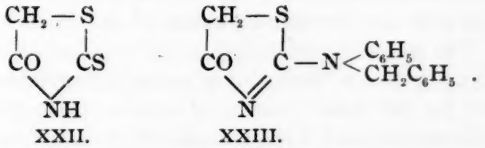
XVII. XVIII.

$HOCOCH_2SC(NH)NHC_6H_5$

XIX.

XX. XXI.

Dixon found that the hydantoïn in question gave α-keto-μ-sulphotetrahydrothiazole ("rhodanininsäure"), formula, XXII below, when heated with carbon disulphide, and he therefore assigned to the compound the structure represented above by formula XVIII. This is undoubtedly correct since by the action of benzyl chloride and alkali, a benzyl derivative is obtained from this hydantoïn, which is identical with that from benzylphenylthiourea, $C_6H_5(C_6H_5CH_2)NCSNH_2$, ethylchloracetate and alkali. This benzyl derivative must have the structure represented by formula XXIII:



XXII. XXIII.

EXPERIMENTAL PART.

I.—*Tertiary Butyl Bromide* $(CH_3)_3CBr$, *and Potassium Thiocyanate.*—The bromide was made by the union of isobutylene and hydrogen bromide. The purified material reacted immediately when warmed with an alcoholic solution of potassium thiocyanate, and potassium bromide separated. The product was an oil which possessed a strong, pungent odor. It could not be distilled under reduced pressure without decomposition and therefore, for analysis, it was simply washed and dried in a desiccator over sul-

phuric acid. A nitrogen determination then gave:

	Calculated for C_5H_9NS.	Found.
Nitrogen	12.17	12.48

Tertiary Butyl Rhodanide and Thioacetic Acid.—Eight grams of the rhodanide and 6 grams of thioacetic acid were heated on the water-bath in benzene for eight hours. On cooling, a white flocculent precipitate separated. This crystallized from benzene in scales or plates, and did not melt at 260°. It was extremely soluble in alcohol, contained nitrogen but no sulphur, and was soluble in a solution of sodium hydroxide. A sufficient amount of this was not obtained for identification. Two determinations gave 10.88 and 11.01 per cent. nitrogen. The oil that remained, after evaporating the benzene, solidified on cooling; it was dissolved in dilute sodium hydroxide and the solution shaken with ether. From the alkaline solution acetic acid precipitated a bright yellow body which, on crystallizing from petroleum ether, melted at 112°-113°. Its solubility in sodium hydroxide, its yellow color and the following nitrogen determination show that this material is *tertiary butylacetyldithiocarbamate,* $CH_3CONHCS.SC(CH_3)_3$.

	Calculated for $C_7H_{13}ONS_2$.	Found.
Nitrogen	7.33	7.32

II.—*1′-Bromisopropyl Benzene,* $C_6H_5CBr(CH_3)_2$, *and Potassium Thiocyanate.*—Isopropyl benzene was prepared from normal propyl chloride and benzene by means of the Friedel-Crafts reaction. The material used boiled at 152°-154° at ordinary pressure. Eight grams of the hydrocarbon were brominated at 115°-120° with the calculated quantity of bromine. The product was washed thoroughly with a solution of sodium carbonate, extracted with ether, and dried in a vacuum. It was impossible to purify this new bromide by distilling under diminished pressure since an attempt at 16 mm. resulted in rapid decomposition taking place at about 135°, with evolution of hydrogen bromide. A bromine determination agreed with the calculated, probably as closely as could be expected.

	Calculated for $C_9H_{11}Br$.	Found.
Bromine	40.20	38.10

This bromide immediately reacted with potassium thiocyanate in warm alcohol, and a fine yellow powder separated. The latter

possessed all the properties of *pseudocyanogen sulphide.* The material remaining in the alcoholic solution proved to be an oil but not enough of this was obtained to establish any definite boiling-point.

III.—*1′,1′-Diphenyl-1′-Bromethane,* $(C_6H_5)_2CBrCH_3$, *and Potassium Thiocyanate.*—Diphenylethane was prepared from ethylidine chloride (from paraldehyde and phosphorus pentachloride) and benzene by means of the Friedel and Crafts reaction. It was found that this hydrocarbon could not be brominated in the usual manner for the preparation of other halogen derivatives of benzene in the side-chain, owing to the ease with which the bromide loses hydrogen bromide. After several unsuccessful attempts it was found that a product consisting essentially of the desired bromide could be prepared by brominating the hydrocarbon at 100°-105°. The product, washed with sodium carbonate and water and dried in a vacuum desiccator, gave the following result on analysis:

	Calculated for $C_{14}H_{13}Br$.	Found.
Bromine	30.6	24.37

When a product thus prepared was distilled at 10 mm. pressure, it rapidly decomposed with evolution of hydrogen bromide. On continuing the distillation, it practically all boiled at 155°-165°. Diphenylethylene boils at 162° at 15 mm. pressure, according to Anschütz.[1] The crude bromide reacted at once with potassium thiocyanate in alcohol, *pseudocyanogen sulphide* separated, and an oil was obtained that boiled at 150°-162° at 11 mm. pressure. (Diphenylethylene?)

IV.—*The Action of Triphenylmethyl Bromide on Potassium Thiocyanate,* which resulted in the formation of a normal thiocyanate, was described in our second paper.[2]

V.—*Ethyl- α -Bromisobutyric Ester Gave Ethylnormalthiocyanisobutyrate,*[3] as shown in this laboratory by Mr. Le B. Gray. The thiocyanate reacts normally with thiobenzoic acid, and *benzoyldithioethyl-α-isobutyrate carbonate,*

$$C_6H_5CONHCS.SC(CH_3)_2CO_2C_2H_5,$$

is formed. This separates from a mixture of benzene and petro-

[1] *Ann. Chem.* (Liebig), **235**, 159.
[2] *Loc. cit.*
[3] *Loc. cit.*

leum ether in the form of yellow prisms, which melt at 113°-114°. It is extremely soluble in alcohol.

	Calculated for $C_{14}H_{17}O_3NS_2$.	Found.
Nitrogen	4.50	4.37

VI.—*Brommethylmalonic Ethyl Ester, $CH_3CBr(CO_2C_2H_5)_2$, and Potassium Thiocyanate.*—Methylmalonic ester was brominated at 65°; the product practically all boiled at 112°-118° at 14 mm. pressure. A bromine determination in a portion of this boiling at 114° gave 31.6 per cent. while the calculated is 31.62 per cent. bromine.

When this bromide was mixed in alcohol with potassium thiocyanate it immediately began to react. The mixture was warmed for about a half hour, on the steam-bath, and then water precipitated an oil possessing a strong penetrating odor. It all boiled at 139°-142° at 9 mm. pressure; a portion boiling at 140° was analyzed with the following result:

	Calculated for $C_9H_{13}O_4NS$.	Found.
Nitrogen	6.06	6.15

Five grams of this rhodanide, 2 grams of thioacetic acid and 10 cc. of benzene were heated on the water-bath for twelve hours. After evaporating the benzene, an oil was obtained which would not solidify in a freezing-mixture. The oil dissolved in a dilute solution of sodium hydroxide and was not precipitated with carbon dioxide; dilute acetic acid, on the other hand, precipitated a yellow solid which was purified by crystallizing from alcohol and benzene. It then formed plates which melted at 124° and showed no effervescence when heated to 175°. Nitrogen determinations agreed with the calculated for *α-keto-μ-sulpho-β-methylthiazolidine:*

	Calculated for $C_4H_5ONS_2$.	Found. I.	Found. II.
Nitrogen	9.52	9.28	9.58

In fact this compound is identical with the so-called "α-rhodaninpropionsäure" of Berlinerblau[1] which was obtained from chlorpropionic acid and ammonium thiocyanate. Berlinerblau gives the melting-point at 123°.

VII.—*α-Bromhydratropicmethyl Ester, $CH_3CBr(C_6H_5)CO_2CH_3$, and Potassium Thiocyanate.*—Although the preparation of hydra-

[1] *Ber. d. chem. Ges.*, **19**, 125.

tropicmethyl ester, by the method which we adopted, includes ten stages, nevertheless the brom-derivative can be more easily obtained, in quantity, by the following procedure than by the method which involves the preparation of atrolactinic acid. On the other hand, a purer product is undoubtedly obtained by the action of hydrogen bromide on atrolactinic acid.[1]

Starting with benzyl chloride we prepared the cyanide, phenylacetic acid, the ethyl ester, and from the latter phenyloxalaceticethyl ester[2] which gave phenylmalonic ester. Eighty grams of this were prepared boiling at 159.5°-160° at 12 mm. pressure. This was methylated[3] and 60 grams of phenylmethylmalonic ester resulted, which boiled at 12 mm. pressure at precisely the same point as the unaltered material. On saponifying this, 21 grams of methylphenylmalonic acid were obtained, melting at 155°-156°. When this was heated and the resulting hydratropic acid was esterified, 13 grams of methyl ester were obtained, which boiled at 218°-221° at ordinary pressure Neure[4] gives the boiling-point of this ester at 221°. The bromination of this was conducted in an oil-bath at 150°. The dark-colored product was washed with water and sodium carbonate and an attempt was made to purify a portion by distilling under diminished pressure, whereupon it was found that the oil underwent decomposition, giving off hydrogen bromide. The washed product was therefore warmed directly with an alcoholic solution of potassium thiocyanate (through an oversight no portion of the oil was reserved for analysis). The products of the reaction consisted of *pseudocyanogen sulphide* and an oil. The latter, since it was not a rhodanide, was not examined.

VIII.—*Tricarbethoxymethyl Bromide, $C.Br(CO_2C_2H_5)_3$, and Potassium Thiocyanate.*—Tricarbethoxymethane was easily brominated on the water-bath and the product boiled, for the most part, at 162°-163° at 16 mm. pressure. The colorless oil thus obtained was analyzed with the following result.

	Calculated for $C_{10}H_{15}O_6Br$.	Found.
Bromine	25.7	25.5

When this bromide was warmed in alcohol with potassium thio-

[1] Fittig and Kast: *Ann. Chem.* (Liebig), **206**, 28 (1881).
[2] Wislicenus: *Ber. d. chem. Ges.*, **27**, 1093.
[3] Wislicenus and Goldstein: *Ibid.*, **28**, 815.
[4] *Ann. Chem.* (Liebig), **250**, 152.

cyanate, it reacted at once and *pseudocyanogen sulphide* separated. On adding water to the alcoholic solution an oil was obtained. This was distilled at 10 mm. pressure and although there was no apparent decompositon, during the distillation, it started to boil at about 141° and continued up to 177°. The bromide therefore reacts with potassium thiocyanate with decomposition.

IX.—*Phenylbrommalonicethyl Ester,* $C_6H_5C.Br(CO_2C_2H_5)_2$, *and Potassium Thiocyanate.*—This bromide was obtained by brominating phenylmalonicethyl ester at 140°-150°. It formed a colorless oil which was found to boil at 192° at 20 mm. pressure and, from another preparation, at 177°-181° at 11 mm. pressure. A bromine determination in the first case gave:

	Calculated for $C_{13}H_{15}O_4Br$.	Found.
Bromine	25.38	24.98

When this bromide was treated with potassium thiocyanate an oil was obtained which could not be purified by distilling under diminished pressure. At 20 mm. rapid decomposition took place at about 200°. The oil, after washing with water and drying, was analyzed with the following result:

	Calculated for $C_{14}H_{15}O_4NS$.	Found.
Nitrogen	4.77	5.37

The nitrogen determination agrees, perhaps as well as could be expected, for a non-rectified oil, with the calculated for *thiocyanphenylmalonicethyl ester,* $C_6H_5C(SCN)(CO_2C_2H_5)_2$.

Ten grams of this rhodanide and 3 grams of thioacetic acid were heated in benzene for twenty-four hours, whereupon, on evaporating the benzene, an oil was obtained which refused to solidify. It was dissolved in cold dilute sodium hydrate and, after standing, was precipitated with dilute hydrochloric acid. This treatment gave a yellow solid, which, on crystallizing from alcohol, formed yellow prisms and melted at 178°-179° without effervescence. A nitrogen determination agreed with the calculated for *α-keto-μ-sulpho-β-phenylthiazolidine:*

	Calculated for $C_9H_7ONS_2$.	Found.
Nitrogen	6.69	6.51

Thiocyanmethylmalonic ester and thiocyanphenylmalonic ester therefore behave in an analogous manner with thioacetic acid and

alkali. The reaction proves that these rhodanides are normal thiocyanates.

X.—*Diphenylchloraceticethyl Ester,* $(C_6H_5)_2C.Cl.CO_2C_2H_5$, *and Potassium Thiocyanate.*—The chlorester was made by treating benzilic acid with phosphorus pentachloride and then pouring the acid chloride into cold alcohol.[1]

When this chloride was warmed in alcoholic solution with potassium thiocyanate for about five hours the reaction was complete. On evaporating, an oil was obtained which had a most remarkable behavior on heating. On attempting to distil under reduced pressure no signs of decomposition could be observed, but no matter at what rate the distillation was conducted it frothed over in one continuous stream, and no fractionation could be accomplished. A nitrogen determination was therefore made in a sample of crude product that was washed and dried over sulphuric acid.

	Calculated for $C_{17}H_{15}O_2NS$.	Found.
Nitrogen.....	4.7	4.2

This rhodanide is distinguished from all others that have been examined by the fact that it does not react with thioacetic or thiobenzoic acids, on warming in benzene for the usual length of time (two to twenty-four hours).

The oil, recovered from the treatment with thiobenzoic acid, was heated with aniline on the steam-bath for from five to six hours. On washing the product with dilute hydrochloric acid and crystallizing from alcohol, colorless prisms were obtained which melted at 250°. This, on analysis, gave the following result which agrees with the calculated for *triphenylpseudothiohydantoin.*

	Calculated for $C_{21}H_{16}ON_2S$.	Found.
Nitrogen.....	8.13	8.14

When this substance was dissolved in alcohol and warmed for a short time with concentrated hydrochloric acid, a product was obtained which crystallized from dilute alcohol in colorless prisms and melted at 144°-145°. An examination of the acid solution showed that aniline had been removed by this treatment and the

[1] Bickel: *Ber. d. chem. Ges.*, **22**, 1537.

crystalline material gave results agreeing with the calculated for *α-μ-diketo-β-diphenyltetrahydrothiazole:*

	Calculated for $C_{15}H_{11}O_2NS$.	Found.
Nitrogen	5.20	5.24

In our second paper on thiocyanates it was shown that ethyl phenylthiocyanacetate reacts with aniline, giving a compound that was considered to be diphenylpseudothiohydantoïn. We now find that ethylphenylchloracetate and phenylthiourea give the same compounds. This proves that these compounds are pseudothiohydantoïns. On boiling the compound from phenylthiourea with 30 per cent. hydrochloric acid a compound was obtained that crystallized from alcohol in needles and melted at 173°-174°. A nitrogen determination agreed with the calculated for *α-μ-diketo-β-phenyl-*N*-phenyltetrahydrothioazole:*

	Calculated for $C_{15}H_{11}O_2NS$.	Found.
Nitrogen	5.20	5.44

Benzylphenylpseudothiohydantoïn.—This was obtained by warming 5.5 grams of phenylpseudothiohydantoïn, 6.5 grams of sodium dissolved in 55 cc. of alcohol and 20 cc. of water, and 3.6 grams of benzyl chloride, until the mixture no longer gave an alkaline reaction. When the alcohol was evaporated, the residue taken up in ether and shaken with alkali, and the product crystallized from alcohol, beautiful, colorless, transparent, square tables were obtained which melted at 124°-125°.

The same compound was obtained by warming 4 grams of unsymmetrical benzylphenylthiourea and 3 grams of ethyl chloracetate, in alcoholic solution, for a number of hours. The alcohol was then evaporated and the residue treated with alkali. On crystallizing from alcohol, square tables melting at 124°-125° resulted and when mixed with the above preparation the melting-point was not altered.

Dixon prepared this benzylphenylpseudothiohydantoïn, by a different method. He states that it melts at 118°-119° (corr.).

NEW HAVEN, CONN.,
April 8, 1902.

NOTES.

Notes upon the Constants of Some Little Known Oils.—

Specific gravity at 22°.

Oil of nigella	0.9093
Oil of boldo leaves	0.9189
Oil of matico	1.1205
Oil of cascarilla	0.9116
Oil of milfoil	0.9217
Oil of wildmint	0.9942 at 20°.

Refractive index at 24° (sodium flame).

Oil of nigella	1.494
Oil of boldo leaves	1.471
Oil of matico	1.513
Oil of cascarilla	1.485
Oil of galanga	1.472
Oil of wildmint	1.487
Oil of milfoil	1.486

Taken with a Bertrand refractometer.

Solubility of the Oils in 80 Per Cent. Alcohol at 22°.

Oil of nigella not perfectly clear in 23 parts of alcohol by volume.

Oil of boldo leaves soluble in 1 or even less volumes.

Oil of matico soluble in 3½ to 4 parts by volume.

Oil of cascarilla, solution not perfect in 20 volumes.

Oil of wildmint soluble in about 1½ volumes.

The oil of wildmint rotates the plane of polarized light to the right 12.59° at 21.7°.

The quantity of these oils was very slight so that no chemical examination could be made. They were distilled by Schimmel & Co., and obtained from Fritsche Brothers, their representatives in the United States.

A. B. AUBERT.

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ORONO, MAINE.

NEW BOOKS.

WATER SUPPLY (Considered principally from a sanitary standpoint). By WILLIAM P. MASON. Third edition. Rewritten. 448 pp. New York: John Wiley & Sons. Cloth. Price, $4.00.

The first edition of this extremely useful book appeared in 1896 and was noticed at length in this Journal. The chapters relating

to methods of chemical and bacterial examination of water which were a part of the earlier edition are now omitted, as they have since been expanded and published as a separate work. Much new matter has been added, however, to this third edition, and all important recent discussions seem to have received attention. At the present time few topics are of greater public interest than are those connected with questions of water purification on the large scale. The chapter dealing with this subject is full of timely information and is quite sufficient to give the general scientific reader a good idea of various practical methods and appliances.

J. H. LONG.

NOTES ON LEAD ORES. By JAMES FAIRIE, F.G.S. London: Scott, Greenwood & Co. 62 pp. 16mo. Price, $1.00.

The book consists of a collection of information concerning all the lead minerals, including occurrence, hardness, specific gravity, blowpipe tests, and composition—just what is to be found in any standard work on mineral[illegible]y. It is well printed in large type.

E. H. M.

GAS AND FUEL ANALYSIS FOR ENGINEERS. A compend for those interested in the economical applications of fuel. By AUGUSTUS H. GILL, S.B., Ph.D. Third edition. New York: John Wiley & Sons. 1902. iv + 104 pp. Price, $1.25.

According to the preface the substance of this book was given in the form of lectures to students in the courses of chemical, mechanical and electrical engineering at the Massachusetts Institute of Technology, Boston.

The author discusses in an exceedingly brief and yet clear and satisfactory manner the common forms of apparatus for technical gas analysis, their manipulation and uses. The methods of taking gas samples, their analysis, the measurement of the temperature of chimney gases, the preparation of reagents, the arrangement of the gas laboratory, and the calorimetric determination of fuel values are treated in separate chapters. Useful calculations in relation to the combustion of fuels together with some valuable tables add to the merits of the book. The illustrations serve fully for the elucidation of the text. The treatment of the subject is excellent and the book can be recommended as a useful aid to students of gas analysis.

F. C. P.

THE AMERICAN YEARBOOK OF MEDICINE AND SURGERY FOR 1902. VOL. I, GENERAL MEDICINE. Philadelphia: W. B. Saunders & Co. 1902. 700 pp. Cloth, $3.00 net. Half morocco, $3.75 net.

This excellent work, which has been issued for a number of years, is under the editorial charge of George M. Gould, M.D., and presents brief summaries of the most important contributions to medical literature made during the preceding year. While naturally intended for practitioners of medicine the book will be found valuable and interesting by those chemists who desire to keep in view the advances in a field closely related to their own in many points. The fundamental importance of chemistry in medicine is becoming more clearly recognized from year to year, and this is well shown by a perusal of the pages of the Yearbook.

J. H. LONG.

INDICATORS AND TEST-PAPERS: Their Source, Preparation, Application, and Tests for Sensitiveness. A Résumé of the Current Facts Regarding the Action and Application of Indicators and Test-Papers Which Have Been Proposed from Time to Time, and are in Present Use in Chemical Manipulation, with a Tabular Summary of the Application of Indicators, Designed for the Use of Chemists, Pharmacists, and Students. BY ALFRED I. COHN, PH.G. Second Edition, Revised and Enlarged. First thousand, New York: John Wiley & Sons; London: Chapman & Hall, Limited, 1902. pp. ix + 267. Price, $2.00.

The first edition of this work which was reviewed in this Journal, 1899, p. 1176, now appears with an appendix containing the description of ten additional indicators in the style of the previous work. The book is a useful addition to the practical chemist's list of dictionaries. References to original articles are unfortunately not given.

The present writer agrees perfectly with the former reviewer in believing that Mohr's unsupported assumption of the cause of color had better have been omitted, and that the isolated discussion of the theory of indicators could well have been improved in the new edition.

W. R. WHITNEY.

A TEXT-BOOK OF INORGANIC CHEMISTRY. BY DR. A. F. HOLLEMAN, rendered into English by HERMON C. COOPER, PH.D. John Wiley & Sons. 1902. viii + 458 pp. Price, $2.50.

The difficult task of incorporating the ideas of the newer physical chemistry with the general descriptive matter necessary in a

text intended to introduce the student to chemical studies has been undertaken by the author of this work with boldness and discretion. The theory is not separated from the facts to which it belongs, but it is in every instance treated as an intimate part of them.

The concept of atoms and molecules is developed at an early stage, after a brief treatment of the properties and composition of water. The kinetic theory, dissociation, law of mass action, methods of determining molecular weights and several related topics are discussed, hand in hand with the description of the elements of the halogen group, and are treated with admirable precision and clearness. The question forces itself, however, upon the reader, whether it is wise to compress so large a part of the theory into the first eighty pages.

The presentation of the principles of thermochemistry is very satisfactory and that of the periodic system is adequate, the customary atomic volume curve being reproduced according to recent data.

A good deal of space is devoted to technological processes, eight pages being given, for example, to the manufacture of sulphuric acid. The few words relating to spectrum analysis could scarcely be improved upon.

The book as a whole has a marked air of scholarly distinction, for which part of the credit belongs to the translator. Very few passages bear any of the ear-marks of translation which too often disfigure American editions of foreign scientific books. While the descriptive matter is subordinated to the consideration of principles, it does not seem to the reviewer that the author has gone too far in this direction. It would not be impossible for some college classes to cover the entire ground of the text in a year's work. LAUNCELOT W. ANDREWS.

A BIBLIOGRAPHY OF THE ANALYTICAL CHRMISTRY OF MANGANESE, 1785–1900. BY HENRY P. TALBOT AND JOHN W. BROWN. City of Washington: Published by the Smithsonian Institution. 1902. pp. viii+124.

This is the fourteenth of the bibliographies pertaining to chemical subjects published by the Smithsonian Institution on recommendation of a Committee of the American Association for the Advancement of Science of which Dr. H. C. Bolton is Chair-

man. For the portion 1785 to 1830 the present Bibliography is based largely on "An Index to the Literature of Manganese, 1596-1874," published by Dr. Bolton in 1875. The present work is, however, confined to the analytical part of the subject and is, apparently, very complete for that field. W. A. N.

JAHRBUCH DES VEREINS DES SPIRITUS-FABRIKANTEN IN DEUTSCHLAND, DES VEREINS DER STÄRKE-INTERESSENTEN IN DEUTSCHLAND UND DER BRENNEREI-BERUFSGENOSSENSCHAFT. Zweiter Jahrgang, 1902. 8vo. xvi + 471 pp. Berlin: Paul Parey. 1902.

This second volume of the Jahrbuch is edited by Dr. Delbruck and its high value to the fermentation and cereal products industries is thereby assured. And this volume certainly establishes the success of the undertaking to publish it.

The editor states in the preface that "the compass of the work has considerably extended this year, not because of prolixity on the part of reporters but because of the enormous increase in material to be treated, and in his oral report to the societies in their general meeting he says "the object of the yearbook is that the members may have the work of the year not in the detached parts of our Journal (Zeitschrift für Spiritus-Industrie) but in a complete volume at the close of the year. * * * * In connection with the Kalendar we publish, this presents a complete compendium of the developments of each new year."

Dr. Delbruck has not exaggerated. It is almost a handbook as well as a yearbook, for nearly every operation in the fermentation, starch and starch derivatives industries is discussed with some suggestion for improvement. From the culture of the potato and barley, the production of malt and yeast, the control of the fermentation and distillation processes, to the separation and utilization of the finished products and wastes, each step has had the attention of specialists appointed to study them and the report in each case is full of valuable information. In addition to the reports from the different sections into which the works of the societies is divided, we are offered most interesting stenographic reports of the general meetings. It would be impossible to recapitulate here what is set forth in the book. It is enough to say that it is filled from cover to cover with facts of the highest scientific and practical value.

Dr. Delbruck intimates that the most important development is that "our investigations have given a new interpretation to the views developed by Buchner, that in the life of yeast we must differentiate *protoplasm*—the seat of life—and *enzyme*—the working constituent (Arbeitstoffe)—of the organism. Their prosecution has now developed facts which will be of importance to the fermentation industries and particularly to physiology. The theme is the struggle of the enzyme in the yeast cell."

The book has a value therefore beyond the boundaries of the industries named and while it should be found in the working libraries of all progressive technologists it will be found useful as a source of valuable suggestion to biologists and physiologists in their work. W. McMURTRIE.

A LABORATORY MANUAL OF PHYSICS FOR USE IN HIGH SCHOOLS. By HENRY CREW, PH.D. AND ROBERT A. TATNALL. New York: The Macmillan Company. 1902. xii + 234 pp. Price, 90 cents, *net*.

The authors have certainly succeeded in producing a very commendable book. The experiments have been carefully selected with a view "to illustrate the first principles of physics as simply as possible," and the directions for their performance are so clear and to the point that much teaching energy is saved. Several new experiments are given as substitutes for the classical ones or to illustrate points hitherto somewhat neglected in elementary physics. The number of experiments is sufficient to admit of some latitude of choice, and by means of references the work in the laboratory is brought into close correlation with seven of the best text-books on elementary physics. There are three appendixes, the first being an interesting reprint from a paper by Robert Boyle on "A New Essay Instrument, etc.", published in 1675, the second giving advice as to the selection of a galvanometer, and the third containing various physical constants. C. E. LINEBARGER.

PLATTNER'S MANUAL OF QUALITATIVE AND QUANTITATIVE ANALYSIS WITH THE BLOWPIPE. Translated by HENRY B. CORNWALL, E.M., Ph.D., assisted by JOHN H. CASWELL, A.M. Eighth edition revised after the sixth German edition, by PROF. FRIEDRICH KOLBECK. Illustrated with 87 wood cuts. New York: D. Van Nostrand Company. 8vo. Cloth. Price, $4.00.

All students of blowpipe analysis will be pleased to have this latest edition of Plattner's classic work in their libraries, especially

when they find that its subject-matter has been kept thoroughly up to date through the labors of Professors Richter, Kolbeck, and others and by valuable foot-notes and suggestions of the translator. Although the blowpipe behavior of several new minerals has been added and some lately devised reactions included, no essential alterations have been made. It is accordingly unnecessary to make an extended review of a work which all will admit is unsurpassed and has been proved in the hands of a generation of students.

The book is divided into three sections:

First, "A Description of Apparatus and Reagents" which is fully illustrated and occupies 56 pages. In this section all apparatus and reagents approved by experience are described.

Second, "Qualitative Blowpipe Analysis." This section occupies the major portion of the book and contains 289 pages. It is complete to the minutest detail and besides the simpler blowpipe reactions gives full directions for separating interfering elements. Here, too, will be found the detailed action before the blowpipe of all minerals and metallurgical products which even the expert is likely to be called upon to identify and for this reason alone the book should be found in every mineralogical laboratory.

Third, "Quantitative Blowpipe Analysis" occupies 94 pages. To the blowpipe enthusiast this section will perhaps prove the most interesting. It is, however, probable that the assayer and chemist will for some time to come monopolize this branch of the subject. Its assays for silver, gold, copper, lead, bismuth, tin, cobalt, nickel, and mercury are highly ingenious and will commend the admiration of all chemists for the intricate knowledge of the chemical reactions involved and their application to the end to be attained.

It seems almost presumptuous to make any criticism of a work of this character but many will regret the omission from the translation of the spectroscopic methods, at least as applied to the ordinary flame spectra. These reactions are surely as applicable to blowpipe work as the many wet methods given, and no procedure gives quicker or more certain results. The chemical notation can hardly be called modern as the old dualistic formulas are still applied to by far the larger number of minerals. All, too, will regret the use of such obsolete terms as sesquioxide, protoxide,

bisulphate of potassa, etc. The work of the translator has, however, been admirably done. The German has been intelligently and accurately converted into excellent English and the paper, typography, and binding are first-class.

The book is well indexed. CHARLES LATHROP PARSONS.

AMMONIA AND ITS COMPOUNDS—THEIR MANUFACTURE AND USES. By CAMILLE VINCENT. Translated from the French by M. T. SALTER. London: Scott, Greenwood & Co. 1901. viii + 114 pp. Price, $2.00.

The author, Camille Vincent, is well known for his method of preparing methyl chloride from the vinasse of the beet-root sugar. In this book he has described in some detail the methods used in France for the production of ammonia and the ammonium compounds. So far as it goes the book is well conceived and well written, but it by no means exhausts the subject and is notable for the almost entire neglect of the commercial side—the cost. One of the large sources of ammonia, the English shales, some of which give 72 pounds of sulphate per ton, is not mentioned. Nor is any attention given to the synthetic preparation of ammonia—a problem now apparently nearing solution. EDWARD HART.